İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF THIOXANTHONE BASED PHOTOINITIATORS VIA CLICK CHEMISTRY

M. Sc. Thesis by
DENİZ TUNÇ

Department : Chemistry

Programme : Chemistry

JANUARY 2011

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DENİZ TUNÇ
(509091036)

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Supervisor (Chairman) : Prof. Dr. Yusuf YAĞCI (ITU)
Members of the Examining Committee : Prof. Dr. Nergis ARSU (YTU)
Prof. Dr. Gurkan HIZAL (ITU)

JANUARY 2011

<u>**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**</u>

‘’CLICK’’ KİMYASI YOLUYLA TİYOKSANTON BAZLI FOTOBAŞLATICILARIN SENTEZİ VE KARAKTERİZASYONU

YÜKSEK LİSANS TEZİ
DENİZ TUNÇ
(509091036)

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Tez Danışmanı : **Prof. Dr. Yusuf YAĞCI (İTÜ)**
Diğer Jüri Üyeleri : **Prof. Dr. Nergis ARSU (YTÜ)**
Prof. Dr. Gürkan HIZAL (İTÜ)

OCAK 2011

FOREWORD

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January 2011 DENİZ TUNÇ
Chemist

TABLE OF CONTENTS

ABBREVIATIONS

^{1}H NMR	: Hydrogen Nuclear Magnetic Resonance Spectroscopy
FT-IR	: Fourier Transform Infrared Spectrophotometer
UV	: Ultra Violet
GPC	: Gel Permeation Chromatography
DSC	: Differential Scanning Calorimetry
FT-IR	: Fourier Transform Infrared Spectrophotometer
ISC	: Intersystem Crossing
CH_2Cl_2	: Dichloromethane
$CDCl_3$	: Deuterated Chloroform
CD_3CN	: Deuterated Acetonitrile
THF	: Tetrahydrofuran
CH_3CN	: Acetonitrile
H_2O	: Water
NaOH	: Sodium Hydroxide
PI	: Photoinitiator
MMA	: Methyl Methacrylate
BA	: Butyl Acrylate
St	: Styrene
AAm	: Acrylamide
TMPTA	: Trimethylolpropane Triacrylate
PI	: Photoinitiator

LIST OF TABLES

Page

LIST OF FIGURES

Page

SYNTHESIZE AND CHARACTERIZATION OF THIOXANTHONE BASED PHOTOINITIATOR VIA CLICK CHEMISTRY

SUMMARY

Photoinitiated free radical polymerization is a well-accepted technology, which finds industrial application in coatings on various materials, adhesives, printing inks and photoresists. Environmental issues involving conventional organic solvents are one of the major concerns in such applications. Photopolymerization in aqueous solution is a highly effective approach to use water instead of the organic solvents.

Type II photoinitiators are a second class of photoinitiators and based on compounds whose triplet excited states are reacted with hydrogen donors thereby producing an initiating radical. Because the initiation based on bimolecular reaction, they are generally slower than Type I photoinitiators, which are based on unimolecular formation of radicals. On the other hand, Type II photoinitiators in general possess better optical absorption properties in the near-UV spectral region.

Typical Type II photoinitiators include benzophenone and derivatives, thioxanthones, benzil and quionones while alcohols, ethers, amines and thiols are used as hydrogen donors. Among Type II photoinitiators, thioxanthone derivatives in conjunction with tertiary amines are efficient photoinitiators with absorption characteristics that compare favorably with benzophenones. Therefore, recent research interest on Type II photoinitiators has mainly focused on the TX- based photoinitiators.

Well established click reaction, metal-catalyzed azide/alkyne click reaction has receieved tremendous interest and been widely used in macromolecular synthetic chemistry.

In this thesis, two different photoinitiators based on thioxanthone anthracene possessing octyl- and poly(ethylene glycol) substituents were added via ‘’click’’ chemistry synthesized and characterized. These efficient photoinitiators exhibited good solublity in organic solvents and water. Their strctural analysis was perofrmed by using ^{1}H-NMR, IR and UV specroscopy. The initiation mechanism was evaluated by means of photo-DSC analysis and photopolymerization experiments.

‘’CLICK’’ KİMYASI YOLUYLA TİYOKSANTON BAZLI FOTOBAŞLATICILARIN SENTEZİ VE KARAKTERİZASYONU

ÖZET

Fotouyarılmış serbest radikal polimerizasyon reaksiyonları çeşitli metaryallerin kaplanması, yapıştırıcılar, yazıcı mürekkepleri ve fotorezistler gibi oldukça geniş bir uygulama alanına sahip olan önemli bir tekniktir. Böylesi uygulamalarda, organik çözücü kullanımını içeren çevresel problemler en büyük endişelerden biridir. Suda gerçekleşen fotopolimerizasyon, organik çözücü yerine suyun kullanımıaçısından oldukça önemli bir yaklaşımdır.

Fotobaşlatıcıların ikinci sınıfı II.tip fotobaşlatıcılardır ve bu tip fotobaşlatıcılar radikal üretimi için uyarılmış enerji düzeyine geçtiği zaman H-verici bileşiklere gereksinim duymaktadırlar. Radikal üretimi iki molekülün etkileşimi sonucu olan, *II. Tip* fotobaşlatıcılar, tek molekülün parçalanarak radikal oluşturduğu *I. Tip* fotobaşlatıcılara göre daha yavaş çalışmaktadır. Diğer yandan, *II. Tip* fotobaşlatıcılar daha iyi optik özelliklere sahip olduklarından, düşük enerjili ışık kaynaklarıyla çalışma imkanı sunmaktadırlar.

Tipik *II. Tip* fotobaşlatıcılar, hidrojen verici bileşik olarak alkol, amin ve tiyoller kullanılırken, benzofenon ve türevleri olan tiyoksanton, benzil ve kuinonu içermektedirler. *II. Tip* fotobaşlatıcılar arasında, tersiyer aminle birleştirilmiş tiyoksanton türevleri, absorbiyon karakterleri benzofenonla karşılaştırılabilen oldukça etkili fotobaşlatıcılardır. Dolayısıyla, son araştırmalar tiyoksanton (TX)-bazlı fotobaşlatıcılar üzerinde yoğunlaşmaktadır.

Uzun zamandır kabul görmüş olan metal katalizli azid/alkin ‘’click’’ reaksiyonu son zamanlarda muazzam bir ilgi görmektedir ve makromoleküler sentetik kimyada oldukça geniş kullanıma sahiptir.

Bu tezde, ‘’click’’ kimyası yoluyla eklenmiş olan oktil- ve poli(etilen glikol) ek gruplarını içeren tiyoksanton antrasen bazlı iki farklı fotobaşlatıcı sentezlenmiş ve karakterize edilmiştir. Bu etkili fotobaşlatıcılar, organik çözücülerde ve suda iyi çözünürlük sergilemektedirler. Yapısal analizleri, ^{1}H-NMR, IR ve UV spektroskopileri tarafından yapılmıştır. Başlatma mekanizmaları ise foto-DSC ve fotopolimerizasyon reaksiyonları tarafından incelenmiştir.

1. INTRODUCTION

In the past several decades, there has been a propelling interest in photoinitiated polymerizations due to the important advantages compare to the corresponding thermal processes [1-5]. Besides low energy requirements, photoinitiated polymerizations provide spatial control and can be turned on and off upon request. Moreover, most polymerization can be carried out in bulk monomers without solvents fulfilling the actual demands of green chemistry. Although of photoinitiated cationic polymerization has gained intensive interest in recent years, the corresponding free radical mode is still the most extensively employed process mainly due to the applicabilty to many monomers and availabilty of wide range of photoinitiators acting at different wavelengths [2,6]. In free radical polymerization, initiating species are formed from organic compounds that can undergo α-cleavage (type I) or hydogen abstraction (type II) reactions. Type II photoinitiators are a second class of photoinitiators based on compounds whose triplet excited states readily react with hydrogen donors, thereby producing initiating radicals (Figure 1) [1, 7, 8, 9].

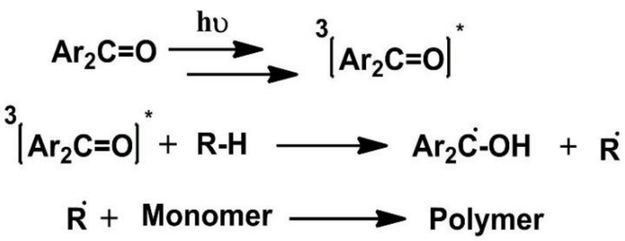


Figure 1.1 : General mechanism for photo-induced polymerization using typicalType II photoinitiator.

Because of the bimolecular radical generation process, they are generally slower than type I photoinitiators, which form radicals unimolecularly. Among various type II photoinitiators, thioxanthone (TX) and derivatives, particularly when used in conjunction with amine hydrogen donors, are efficient photoinitiators owing to their absorption characteristics that favorably compare with benzophenones. In our group, we have focused on the developments of new strategies to improve the efficiency of TX photoinitors. For example, we recently reported the use of several derivatives of thioxanthone, namely thiol and carboxylic acid derivatives as photoinitiators for free radical polymerization [10-14]. A major advantage of these initiators is related to their one component nature. They can serve as both a triplet photosensitizer and a hydrogen donor. Thus, these photoinitiators do not require an additional coinitiator, i.e., a separate molecular hydrogen donor. In another studies, the problems associated with migration of low molar mass photoinitiators or their photofragments were overcome by preparing polymeric thioxanthone and benzophenone photoinitiors. It was also reported that the spectral sensitivity of TX based photoinitiators can be extented to visible range by incorporating polynuclear aromatic moieties into TX structure such as anthracene, fluorene and carbozale groups [10, 15, 16]. It was found that the anthracene derivative, TX-A initiates the polymerization in a different way than the tradional type II mechanism [15]. Although the absorption spectra of TX-A reflects characteristics of both chromophores, the anthracene moiety is the dominant part in the formation of initiating radicals. This photoinitiator also enables further modification through Diels-Alder reaction of the anthacene group present in the structure. This way, polymeric TX photoinitiators based on polystyrene and poly(ethylene oxide) were prepared [17, 18].

Well established click reaction, metal-catalyzed azide/alkyne click reaction has receieved tremendeous interest and been widely used in macromolecular synthetic chemistry [17, 18].

Although TX-A is an efficient photoinitiator for free radical polymerization even in the presence of oxygen, it suffers from the low solubility in neat monomers and non-polar solvents which limits its use in practical applications [15].

In this thesis, we describe the use of copper catalyzed azide-alkyne ‘’click’’ chemistry [19] to modify TX-A photoinitiator with long alkoxy or poly(ethylene glycol) chains. Detailed polymerization investigations both in the presence and absence of co-initiator amines in acrylic resins shows to be very efficient in initiating acrylate polymerization. Most importantly, the initiators are soluble in monomers, polar and nonpolar solvents, and water that facilitiates to conduct the polymerization in bulk, solution and water. The structures of the products are characterized by various analysis including ^{1}H-NMR, IR, UV, floresans and photo-DSC analysis.

2. THEORETICAL PART

2.1 Photopolymerization

Photoinitiated polymerization has been widely used in the electronics industry for etching, microlithography, in paper industry for printing or in polymer industry for curing processes as well as several other applications. These commercial needs lead to increasing of demand of suitable photoreaction conditions for ‘’green’’ chemistry.

2.2.1 Photoinitiated Free Radical Polymerization

Photoinitiated free radical polymerization consists of photoinitiation, propagation, chain transfer, and termination (Figure 2.1). Particularly, the role that light plays in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating radicals. The reaction of these radicals with monomer, propagation, transfer and termination are purely thermal processes; they are not affected by light [20].

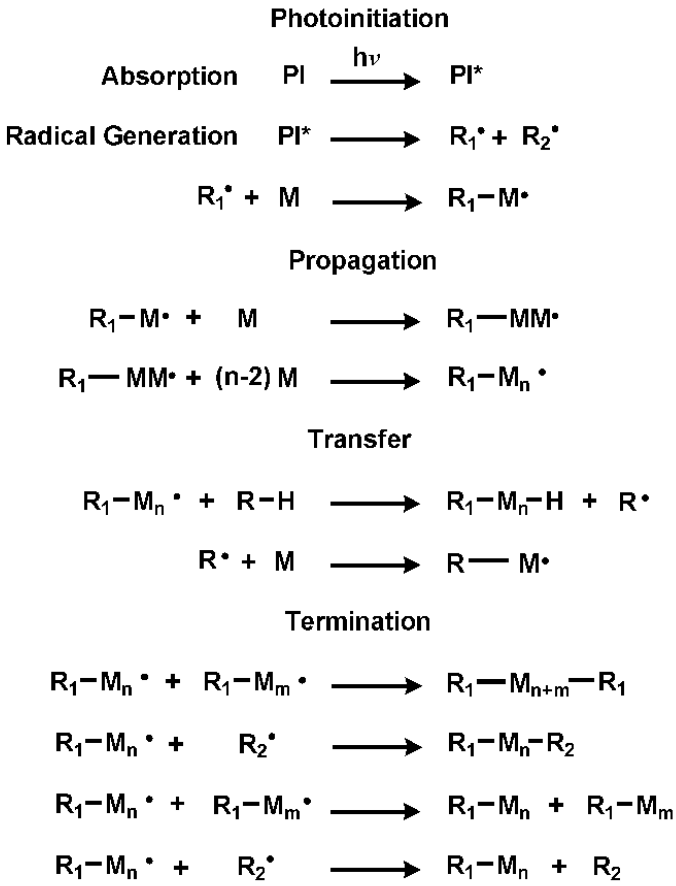


Figure 2.1 : General photopolymerization mechanism.

Photoinitiation involves absorption of light by a photosensitive compound or transfer of electronic excitation energy from a light absorbing sensitizer to the photosensitive compound. Homolytic bond rupture leads to the formation of a radical that reacts with one monomer unit. Repeated addition of monomer units to the chain radical produces the polymer backbone (propagation).

Chain transfer also takes place, that is, growing chains are terminated by hydrogen abstraction from various species (e.g., from solvent) and new radicals capable of initiating other chain reactions are formed.

Finally, chain radicals are consumed by disproportionation or recombination reactions. Termination can also occur by recombination or disproportionation with any other radical including primary radicals produced by the photoreaction.

2.2.1.1 Absorption of light

Photochemistry is concerned with chemical reactions induced by optical radiation [21]. The radiation is most often ultraviolet (200–400 nm) or visible (400–800 nm) light but is sometimes infrared (800–2500 nm) light.

The absorption of a photon of light excites the electrons of a molecule. The stability of bond of compound is reduced by electronic excitation, under this circumstance, lead to its dissociation.

Chromophoric groups defined as having functional group which show high absorbency. For example, phenyl rings or carbonyl groups take place in this groups. The energy causing excitation, E, is described by $E=hc/\lambda$ where h is Planck's constant, c is the speed of light, and , λ is the wavelength of the exciting light. Light absorption is described by $A= \varepsilon C l$, where ε is the molar absorptivity (extinction coefficient), C is the concentration of the species, and l is the light path length.

2.1.1.2 Initiators for free radical photopolymerization

Most of photoinduced reactions are carried out by using photoinitiators in order to generate radicals. A photoinitiator is a molecule that absorbs energy of radiation, and consequently initiates polymerization. Photoinitiators are generally divided into two classes according to the process by which initiating radicals are formed. Type I photoinitiators and Type II Photoinitiators.

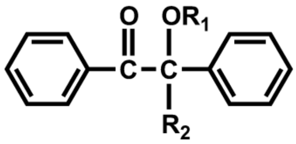
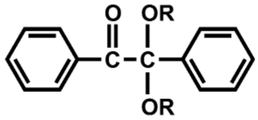
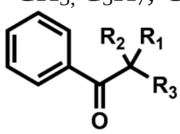
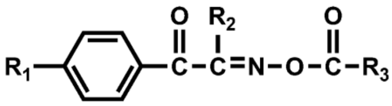
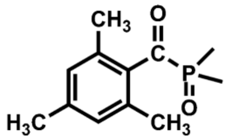
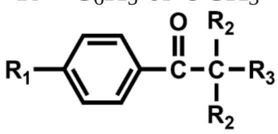
Type I Photoinitiators: Unimolecular Photoinitiators

Compounds which undergo unimolecular bond cleavage upon irradiation as shown in Eq. 2.1 are termed "*Type I* photoinitiators". This process is termed homolytic cleavage or direct fragmentation. The fragmentation that leads to the formation of radicals is, from the point of view of chemical kinetics, a unimolecular reaction.

$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{PI}^* \xrightarrow[\text{fragmentation}]{\text{unimolecular reaction}} \underbrace{R_1^{\bullet} + R_2^{\bullet}}_{\text{free radicals}} \qquad \textbf{(2.1)}$$

There are many photoinitiators which are classified as most efficient Type I photoinitiators, and are termed as benzoin ether derivatives, benzil ketals, hydroxylalkylphenones, α-aminoketones and acylphosphine oxides. Examples of them are given in the Table 2.1 [22].

Table 2.1: Main Type I photoinitiators for free radical polymerization.

Photoinitiators	***Structure***	***λ_{max} (nm)***
Benzoin ethers	 R_1 = H, alkyl R_2 = H, substituted alkyl	323
Benzil ketals	 R = CH_3, C_3H_7, CH_2	365
Acetophenones	 R_1 = OCH_3, OC_2H_5 R_2 = OCH_3, H R_3 = C_6H_5, OH	340
Benzyl oximes	 R_1 = H, SC_6H_5 R_2 = CH_3, C_6H_{13} R_3 = C_6H_5, OC_2H_5	335
Acylphosphine oxides	 R = C_6H_5 or OCH_3	380
Aminoalkyl phenones	 R_1 = SCH_3, morpholine R_2 = CH_3, CH_2Ph or C_2H_5 R_3 = $N(CH_3)_3$, morpholine	320

Type II Photoinitiators: Bimolecular Photoinitiators

When certain compounds absorb light leading to excited state molecules, they do not undergo Type I reactions because their excitation energy is not high enough for fragmentation (i.e., their excitation energy is lower than the bond dissociation energy). The photoinitiator that absorbs the light and a co-initiator that serves as a hydrogen or electron donor. The excited state photoinitiator interacts with the coinitiator (COI), to generate initiating radicals in a bimolecular reaction as shown in Eq. 2.2, the initiating system is termed a "Type II Photoinitiator".

$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{PI}^{*} + \mathrm{COI} \xrightarrow[\text{hydrogen abstraction}]{\text{bimolecular reaction}} \underset{\text{free radicals}}{R_1^{\bullet} + R_2^{\bullet}} \qquad \textbf{(2.2)}$$

In Type II systems, radicals are generated by two distinct pathways: hydrogen abstraction and photo-induced electron transfer process.

Hydrogen abstraction

Photoinitiators that proceed via a hydrogen abstraction mechanism are exemplified by combination of benzophenone and a hydrogen donor (Figure 2.2) When R-H is an amine with transferable hydrogen, benzophenone undergoes an electron transfer followed by a hydrogen abstraction to produce an initiating species and semipinacol radical. The semipinacol radical does not efficiently initiate polymerization and typically react with other radicals in the system as a terminating species causing a reduction in the polymerization rate.

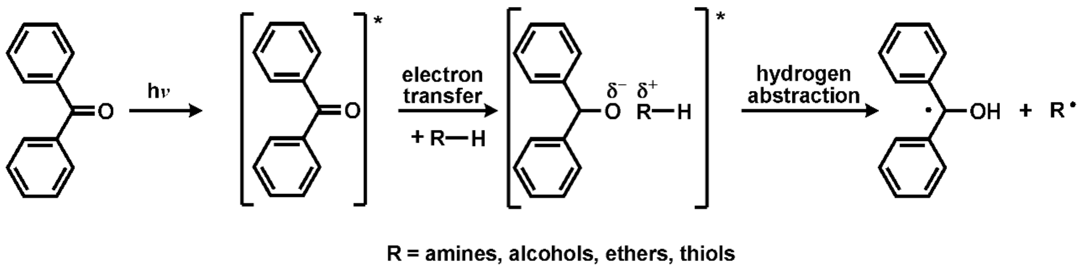
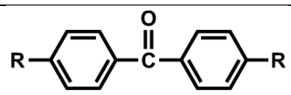
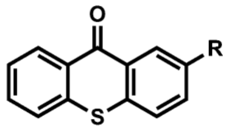
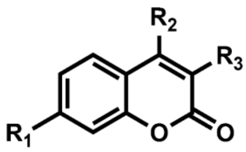
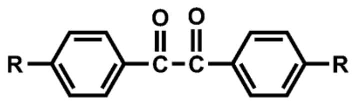


Figure 2.2 : Photo-induced free radical formation upon irradiation of benzophenone in the presence of hydrogen donor

Table 2.2: Type II free radical photoinitiators.

Photoinitiators	Structure	λ_{max} (nm)
Benzophenones	 R = H, OH, $N(C_2H_5)_2$, C_6H_5	335
Thioxanthones	 R = H, Cl, isopropyl	390
Coumarins	 $R_1 = N(C_2H_5)_2$, $N(CH_3)_2$ $R_2 = CH_3$, cyclopentane R_3 = benzothiazole, H	370
Benzils	 R = H, CH_3	340

Type II photoinitiators including benzophenones, thioxanthones, benzyls, and ketocoumarins are listed in Table 2.2

Photolysis of aromatic ketones, such as benzophenone, thioxanthones, benzil, and quionones, in the presence of hydrogen donors, such as alcohols, amines, or thiols, leads to the formation of a radical produced from the carbonyl compound (ketyl type radical) and another radical derived from the hydrogen donor. The photopolymerization of vinyl monomers is usually initiated by the radical produced from the hydrogen donor. The ketyl radicals are usually not reactive toward vinyl monomers due to the steric hindrance and the delocalization of unpaired electron. The overall mechanism of the photoinitiation is represented in Figure 2.3 on the example of thioxanthone.

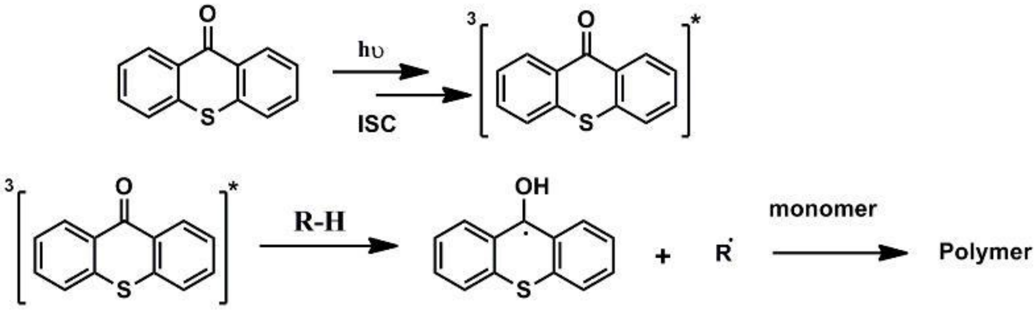
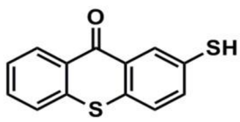
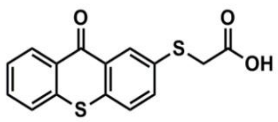
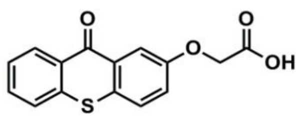
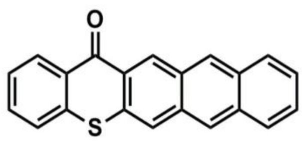
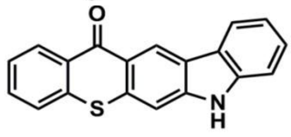


Figure 2.3 : Photo-initiated free radical polymerization using thioxanthone.

One of the disadvantages of Type II systems concerns high usage of high volatile and odorous amines as hydrogen donors [23]. Poly(ethylene oxide) and poly(ethylene imine) based dendrimers of the following structures have been successfully used as polymeric hydrogen donors to replace low molecular weight amines in the formulations.

Table 2.3: Thioxanthone based one-component photoinitiators.

Photoinitiator	Structure	Mode of Action	Ref.
2-Mercaptothioxanthone		Hydrogen abstraction	[14]
2-(9-Thioxanthone-2-thio) acetic acid		Intramolecular radical generation	[13]
2-(9-Thioxanthone) acetic acid		Intramolecular radical generation	[24]
Thioxanthone-anthracene		Endoperoxide formation	[15]
Thioxanthone-carbazole		Hydrogen abstraction - Intramolecular	[16]

2.3 Thioxanthones

Thioxanthones in conjunction with tertiary amines are efficient photoinitiators [23] with absorption characteristics that compare favorably with benzophenones; [10] absorption maxima are in the range between 380 to 420 nm (ε = 104 L mol^{-1} cm^{-1}) depending on the substitution pattern. The reaction mechanism has been extensively investigated by spectroscopic and laser flash photolysis techniques [13, 14, 24]. It was found that the efficiency of thioxanthones in conjunction with tertiary amines is similar to that of benzophenone/amine systems. The most widely used commercial derivatives are 2-chlorothioxanthone and 2-isopropylthioxanthone. A great advantage is that thioxanthones are virtually colorless and do not cause yellowing in the final products.

More recently, one component bimolecular photoinitiator systems based on the decarboxylation process were reported by Aydin et al [25].

Recently, Yagci and co-workers prepared and studied the initiation mechanisms of different thioxanthone derivates with absorbtions at the visible and/or near UV range. They display photoactivity without an additional H-donor compound. Espacially the case of anthrecene-thioxanthone is really interesting as it initiates free radical polymerization in the presence of air. The initiation mechanism is followed in Figure 2.4.

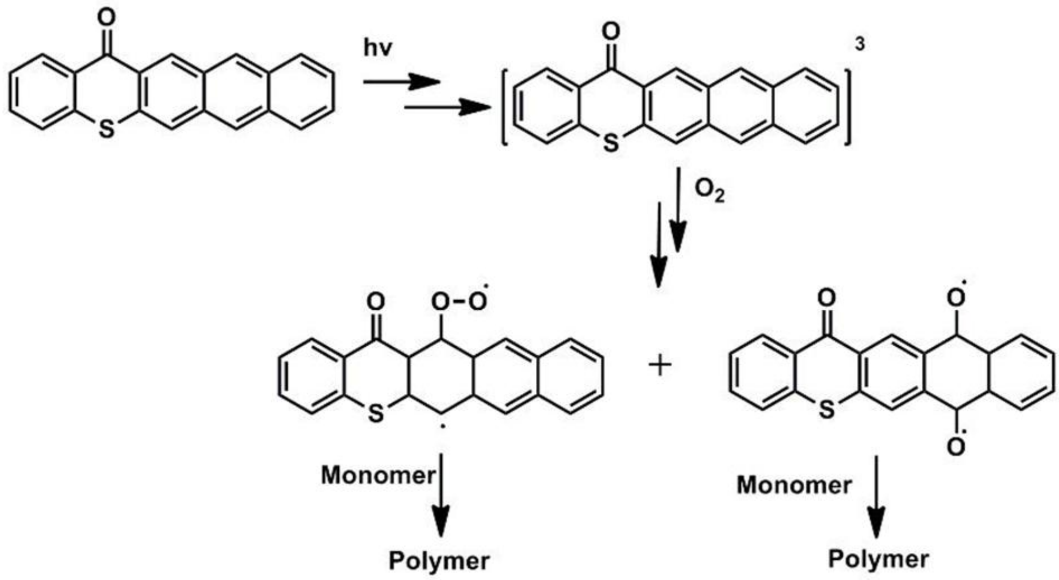


Figure 2.4 : Photoinitiated free radical polymerization by using TX-A

TX-A is also an efficient photoinitiator for free radical polymerization. This photoinitiator does not require an additional hydrogen donor for radical formation and initiates the polymerization of both acrylate and styrene monomers in the presence of air. In addition, TX-A possesses excellent optical absorption properties in the near-UV spectral region, ensuring efficient light absorption from most UV-curing tools. These properties suggest that TX-A may find use in a variety of practical applications.[15]

Yagci group also reported the synthesis of a one-component Type II macrophotoinitiator for free-radical polymerization via DA click reaction. The obtained photoinitiator, possessing both light absorbing and hydrogen donating sites as in the same structure, is able to polymerize hydrophilic vinyl monomers without the requirement of an additional coinitiator. The water solubility of PEG provides the use of initiating system in water-borne formulations. These properties suggest that the polymeric photoinitiator may find use in a variety of practical applications. [17]

2.4 Click Reactions

The reaction that gives opportunity to attach ligands onto polymers for modification is called click reaction and it is also known as Sharpless 'click' reaction [26, 27]. This modification process provides; a) often quantitative yields, b) a high tolerance of functional groups c) an insensitivity of the reaction to solvents and d) reaction at various types of interfaces such as solid/liquid, liquid/liquid, or even solid/solid interfaces [27, 28]. Click reactions are preferable reactions for modification because of moderate reaction conditions, high yields, short periods of reaction times and high selectivity [29-31]. There is a wide range of application field of this reaction, which varies with the sort of polymers [31]. Click reactions enabled the C-C bond formation in a quantitative yield without side reactions and requirement for additional purification steps. Click reactions are particularly important in preparative methods, in which high conversion of functional groups is desirable [32-34]. Numerous applications of click chemistry in polymer science as well as molecular biology and nanoelectronics have recently been reviewed [18, 29, 35].

Click reactions are derivatives of Huisgen 1, 3 dipolar cyloaddition reactions and occurs between terminal acetylenes and azides by metal catalyst at room temperature (See Figure 2.23) [26, 36, 37]. Ru, Ni, Pt, Pd and especially Cu (I) species can be used as catalyst for click reactions [30, 31, 38]. As stated by several authors, these metals speed up the reactions [30-31].

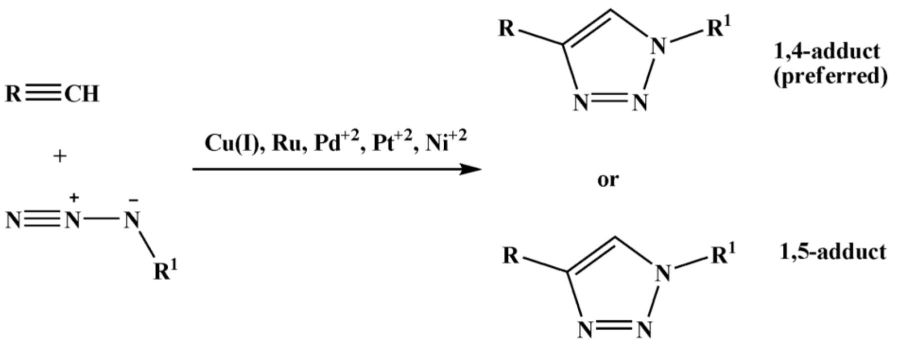


Figure 2.5 : Azide/alkyne-type click reactions

2.4.1 Suitable Compounds for Click Reactions

Exceptions of self-reactive reagents and materials that can produce stable complexes with Cu (I), all functional groups are suitable for click reactions [39-41]. The figure shows the compounds, which are not suitable for, azide/alkyne-type click reactions because of the Huisgen 1, 3 dipolar cyloaddition side reactions [41-43].

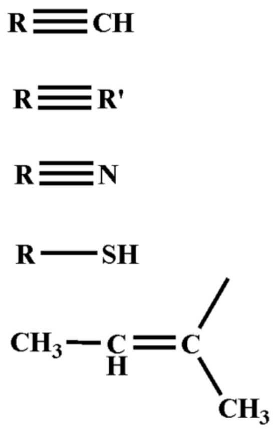


Figure 2.6 : Unsuitable compounds for azide/alkyne type click reaction

2.4.2 Mechanism of Click Reactions

As it mentioned before click reactions occurs between terminal acetylenes and azide by metal catalyst. The mechanism of click reactions first explained by Meldal and co-workers and Sharpless and co-workers [39, 44, 45]. Multifarious catalytic systems are present to affect the 1, 3-dipolar cycloaddition process. Cu (I) salts can be directly used or Cu (I) species can be obtained from the reduction of Cu (II) by sodium ascorbarte or metallic copper in catalytic systems [39, 45, 46]. The mechanism of click reactions, shown below, depends on the Cu-acetylide formation [39, 45].

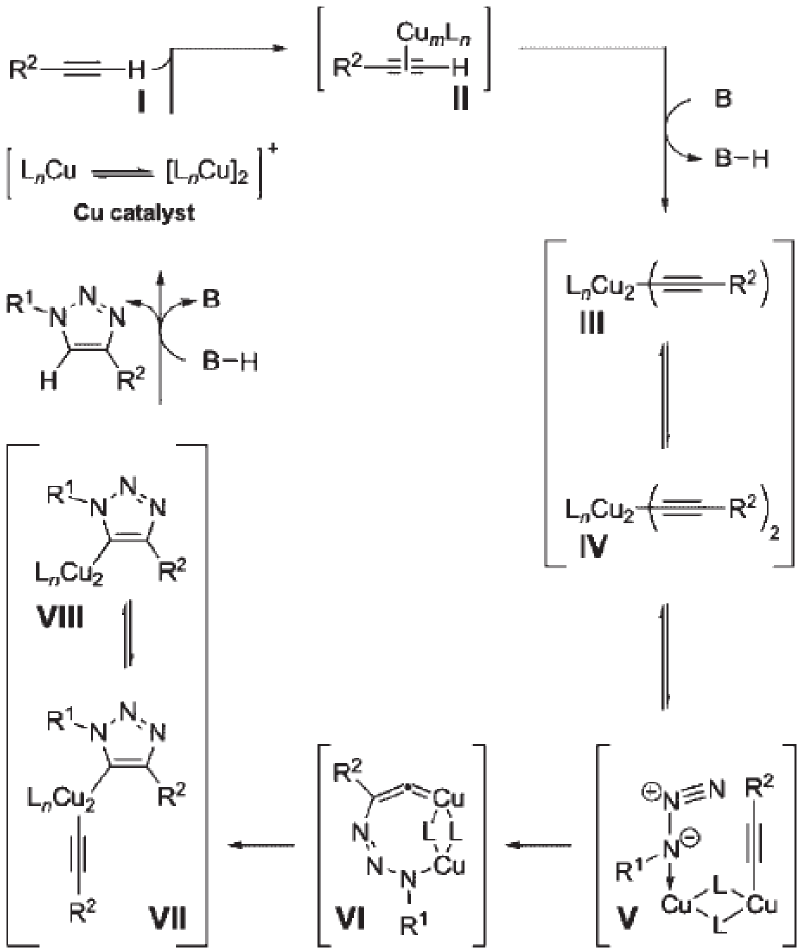


Figure 2.7 : Mechanism of click reaction

Terminal alkynes and Cu (I) particles produce a π-complex (Cu-acetylide) to lower pKa value of the terminal alkynes that allow attack onto C-H bond [31, 47, 48]. In addition, 1-5 equivalents of base have positive influences on the formation of the copper (I)-acetylide. THF, diethyl ether, DMF, DMSO or halogenated solvents are applicable for click reactions. And also, water/alcohol or water/toluene systems can give excellent results [47-49].

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

Styrene (St, 99%, Aldrich): It was passed through a basic alumina column to remove the inhibitor before use.

Methyl methacrylate (MMA, 99%, Aldrich): It was passed through a basic alumina column to remove the inhibitor before use.

Butyl acrylate (BA, ≥99%, Aldrich): It was passed through a basic alumina column to remove the inhibitor before use.

Acryl amide (AAm, Fluka): It was used as received.

3.1.2 Solvents

Dichloromethane (J.T. Baker): It was used as recieved.

Methanol (Technical): It was used for the precipitation of polymers without further purification.

Ethanol (Riedel-de Haën): It was used for the crystallization of a monomer without further purification.

Toluene (99.9%, Sigma-Aldrich): It was dried with calcium chloride and distilled over sodium wire.

Tetrahydrofuran (THF, 99.8%, J.T.Baker):

(a) It was used as eluent for chromatography as received (High Performance Liquid Chromatography Grade).

(b) For use in the chemical reactions, it was dried and distilled over benzophenone/sodium.

n-Hexane (95%, Aldrich): It was used without further purification.

Diethyl ether (J.T. Baker): It was used as recieved.

Acetonitrile (98%, Aldrich): It was used without further purification.

Acetone (99%, Carlo Erba): It was used without further purification.

3.1.3 Other chemicals

Anthracene (99%, Acros): It was used without further purification.

Thiosalysilic acid (97%, Sigma-Aldrich) : It was used without further purification.

Sodium hydroxide (NaOH, Riedel-de Haën): It was used as received.

n-Butyl lithium (nBuLi, Acros): It was used as received.

Triethylamine (Acros): It was used as received.

Trimethylolpropane triacrylate (TMPTA, 99%, Sigma-Aldrich) : It was used as recieved.

Sulfuric acid (H_2SO_4, 95-97%, Fluka) : Sulfuric acid was used as recieved.

Hydrogen bromide (HBr, ≥ 99 %, Aldrich): It was used as received.

Sodium borohydride ($NaBH_4$, Aldrich): It was used as received.

N,N'-Dicyclo hexylcarbodiimide(DCC, 99%, Aldrich *) :* It was used as received.

4-Dimethylaminopyridine (DMAP, 99%, Acros): It was used as received.

*Pentynoic acid (*99%, Aldrich) : It was used as received.

Poly(ethylene glycol) monomethylether (Me-PEG, Mn: 500, Fluka) : It was used as received.

Azidotrimethylsilane (TMS-N_3, Fluka) : It was used as received.

Tert-Butyl Nitrite (t-BuONO, Aldrich) : It was used as received.

L-ascorbic acid sodium salt (99%, Acros): It was used as received.

3.2 Equipments

3.2.1 Photoreactor

A Rayonet type photoreactor equipped with 16 Philips 8W / O6 lamps emitting light nominally at 350 nm was used.

3.2.2 ^{1}H Nuclear magnetic resonance spectroscopy (^{1}H-NMR)

^{1}H-NMR spectra of 5–10 % (w/w) solutions in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard were recorded at room temperature at 250 MHz on a Bruker DPX 250 spectrometer.

3.2.3 Infrared spectrophotometer (FT-IR)

FT-IR spectra were recorded on a Perkin-Elmer FTIR Spectrum One spectrometer via attenuated total reflectance (ATR) technique with 4 scans for each sample.

3.2.4 UV-Visible spectrophotometer

UV-Visible spectra were recorded on a Shimadzu UV-1601 UV-visible spectrophotometer.

3.2.5 Differential Scanning Calorimeter (DSC)

Differential scanning calorimeter (DSC) was performed on a Perkin Elmer Diamond DSC with a heating rate of 10 ^{o}C min^{-1} under nitrogen flow.

3.2.6 Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector and Viscotek a differential refractive index (RI) detector. Three ViscoGEL GPC columns (G2000H_{HR}, G3000H_{HR} and G4000H_{HR}), (7.8 mm internal diameter, 300 mm length) were used in series. The effective molecular weight ranges were 456–42,800, 1050–107,000, and 10,200–2,890,000, respectively. THF was used as an eluent at flow rate of 1.0 mL min^{-1} at 30°C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. Molecular weights were calculated with the aid of polystyrene standards.

3.2.7 Fluorescence spectrophotometer

Fluorescence and phosphorescence measurements were performed on a Jobin Yvon-Horiba Fluoromax-P spectrophotometer.

3.3 Preparation Methods

3.3.1 Synthesis of Thioxanthone-Anthracene (5-Thiapentacene-14-one) (TX-A).

Thioxanthone-anthracene (TX-A) (5-thiapentacene-14-one) was synthesized according to the literature procedure [15]. ^{1}H NMR (250 MHz) in $CDCl_3$: δ 8.86 (s, 1H), 8.61–8.64 (d, 1H), 8.42–8.45 (t,1H), 8.35 (s, 1H), 7.96–8.1 (m, 2H), 7.82–7.91 (d, 1H), 7.44–7.72 (m, 5H). FTIR %*T* (cm^{-1}): 3050, 1672, 1622, 1593, 1339, 1147, 956, 883, 725.

3.3.2 Synthesis of TX-A-NO_2

TX-A (50 mg, 0.16 mmol) was dissolved with 0,5ml glacial acetic acid at room temperature for 10min. %70 HNO_3 (0,0114 ml, 0.16 mmol) was slowly added to this mixture and they were stirred for 30 min.(until clear solution) in ice-bath and then reaction mixture was filtered and obtained NO_2-TX-A was precipitiated in mixture of HCl (%37, 0.071ml) and equal mole of glacial acetic acid and then yellow TX-A-NO_2 precipitate was obtained. This precipitate was washed with glacial acetic acid (gAA) twice and with water until obtain neutral substance. This substance was dissolveed in hot %10 NaOH (0.16mmol, 0.0857 ml) at 60-70^{o}C and washed with %10 NaOH (warm) and then water, dried, recrystalled from gAA. Finally, obtained orange-yellow TX-A-NO_2 was characterized by ^{1}H-NMR and IR with %90 yield (45 mg, 357.38 g/mol) .

3.3.3 Reduction of TX-A-NO_2

TX-A-NO_2 (45 mg, 0.126 mmol) and HCl (9.95 µl, 0.126 mmol), and distilled water (494 µl, 0.126 mmol), Fe^o (302.4 mg, 0.126 mmol) were mixed in ethanol (3 ml) at 90^{o}C for 90min. And after 90 min. solution was filtered when it was hot. After drying obtained TX-A-NH_2 characterized by ^{1}H-NMR and IR with %80 yield (36 mg, 329.41 g/mol).

3.3.4 Synthesis of TX-*A*-N_3

TX-A-NH_2 (36 mg, 0.109 mmol), and tert-butyl nitrite (t-BuONO) (19.32 µl, 0.109 mmol) were dissolved in dried THF and azidotrimethylsilane (TMS-N_3) (17.3 µl, 0.109 mmol) was added dropwise for 1 hour and mixture was stirred for 2 hours in ice-bath under nitrogen. And then reaction mixture was concentrated under vacuum, washed with THF, and dried, and characterized by ^{1}H-NMR and IR. TX-A-N_3 was obtained with %88 yield (32 mg, 353,40 g/mol).

3.3.5 Synthesis of Propargyl Functional Octane (Oct-Pro)

Propargyl alcohol (0.035 mol, 2,107 ml), NaH (39,16 mmol, 0,93 g) were mixed with 10-20 ml dried THF under nitrogen in ice-bath for 2 hours and then bromooctane (6.81 ml, 4.6 mmol) was added and, stirred 24h. at room temperature and, refluxed at room temperature for 3 hours. Obtained substance was characterized by ^{1}H-NMR and IR.

3.3.6 Synthesis of Octyl Functional Thioxanthone-Anthracene (TX-A- Oct)

TX-A-N_3 (30 mg, 0.085 mmol) and Oct-Pr (8.72 mg, 0.085 mmol) were mixed in dried THF under nitrogen atmosphere. After mixing, CuBr (12.23 mg, 0.081 mmol), PMDETA (18.85 µl, 0,085 mmol) were added and stirred for 40 min. in ice-bath still under nitrogen atmosphere, and then reaction solution was stirred at room temperature over night. Obtained TX-A-Oct was filtered over Al_2O_3 and washed with THF and concentrated, and dried finally characterized by ^{1}H-NMR and IR. Yield was %87 (27 mg)

3.3.7 Preparation of Alkyne Functional PEG (Alkyne-PEG) [50].

PEG (Mn: 500 g/mol, 1.5 g, 3 mmol) was dissolved in 25 mL of CH_2Cl_2. 4-Pentynoic acid (0.44 g, 4.5 mmol) and DMAP (0.36 g, 3 mmol) were successively added to the reaction mixture. After stirring 5 min at room temperature, a solution of DCC (0.92 g, 4.5 mmol) in 15 mL of CH_2Cl_2 was added to the reaction mixture and stirred overnight at room temperature. After filtration of the salt, the solution was concentrated and product was purified by column chromatography over silica gel eluting with CH_2Cl_2/ethyl acetate mixture (1:10) and then with CH_2Cl_2/MeOH (10:1). Finally, concentrated solution of alkyne-PEG was precipitated in diethyl ether and filtered.

3.3.8 Synthesize of PEG Functional Thioxanthone Anthracene (TX-A-PEG)

TX-A-N_3 (30 mg, 0.085 mmol) and Alkyne-PEG (80.5 mg, 0.085 mmol) were mixed in dried THF under nitrogen atmosphere. After mixing, CuBr (12.23 mg, 0.081 mmol), PMDETA (18.85 µl, 0,085 mmol) were added and stirred for 40 min. in ice-bath still under nitrogen atmosphere, and then reaction solution was stirred at room temperature over night. Obtained TX-A-Oct was filtered over Al_2O_3 and washed with THF and concentrated, and dried finally characterized by ^{1}H-NMR and IR. Yield was %86 (26 mg)

3.3.9 General procedure for photopolymerization

Appropriate solutions of photoinitiator and different monomers (MMA, AAM, BA, St) were irradiated in photoreactor equipped with 12 Philips lamps emitting nominally at λ=350 nm for 90 min in the presence and absence of triethylamine (TEA) in either an air or N_2 atmosphere. Polymer formed at the end of irradiation was precipitated in 10-fold excess methanol and dried in vacuo. The conversion % was calculated gravimetically for all samples.

3.3.10 Photocalorimetry (Photo-DSC)

The photo-differential scanning calorimetry (Photo-DSC) measurements were carried out by means of a modified Perkin-Elmer Diamond DSC equipped with a high pressure mercury arc lamp (320–500 nm). A uniform UV light intensity is delivered across the DSC cell to the sample and reference pans. The intensity of thelight was measured as 53 mW cm-2 by a UV radiometer capable of broad UV range coverage. The mass of the sample was 3 mg, and the measurements were carried out in an isothermal mode at 30°C under a nitrogen flow of 20 mL min-1. The reaction heat liberated in the polymerization was directly proportional to the number of acrylate groups reacted in the system. By integrating the area under the exothermic peak, the conversion of the acrylate groups (*C*) or the extent of the reaction was determined according to eq 3.1:

$$C = \Delta H_t / \Delta H_0^{\text{theory}} \qquad \textbf{(3.1)}$$

where ΔHt is the reaction heat evolved at time t and ΔH_0 theory is the theoretical heat for complete conversion. ΔH_0theory = 86 kJ mol^{-1} for an acrylic double bond [51] . Therate of polymerization (*R*p) is directly related to the heat flow (d*H*/d*t*) by eq 3.2:

$$R\text{p} = \mathrm{d}C / \mathrm{d}t = (\mathrm{d}H / \mathrm{d}t) / \Delta H_0^{\text{theory}} \qquad \textbf{(3.2)}$$

4. RESULTS AND DISCUSSION

4.1 Synthesis and Characterization of the Photoinitiators

The click components, namely azide-functional photoinitiator and alkyne-functional subsitizing molecules were synthesized separately. Accordingly, synthesized TX-A [15]. was first reacted with HNO_3/HCl and then with aqueous NaOH to yield nitro functional TX-A which was subsequently reduced to amino functional TX-A (TX-A-NH_2) by using Fe/HCl. Following the literature procedure, the amino groups were converted to azide to yield the desired product (TX-A-N_3). The overall azidation process is presented in Figure 4.1.

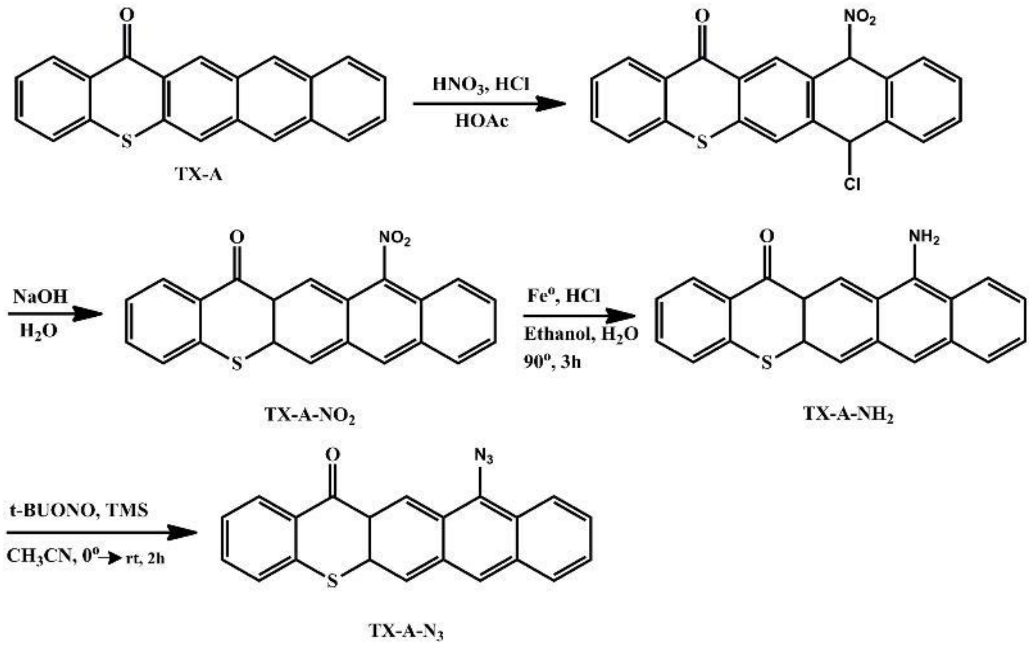


Figure 4.1 : Synthesis of TX-A-N_3.

The structures of the intermediates and final product were confirmed by ^{1}H NMR spectra ($CDCl_3$) (Fig 4.2). The aromatic protons of phenyl groups emerge at around 8 ppm, due to the electron withdrawing effect of the –NO_2. The reduction process led to two changes in the spectra. While N–H protons appeared at 5.30 as new peaks, the aromatic peaks resonate at lower magnetic fields in the range of 8.1–6.8 ppm.

The integration ratios of N–H protons to aromatic C–H protons are 2:11, respectively, indicating quantitative reduction of the nitro groups to amino groups. The efficient transformation of TX-A-NO_2 to TX-A-N_3 was also evidenced from ^{1}H NMR spectrum wherein the resonance due to N–H protons disappeared completely.

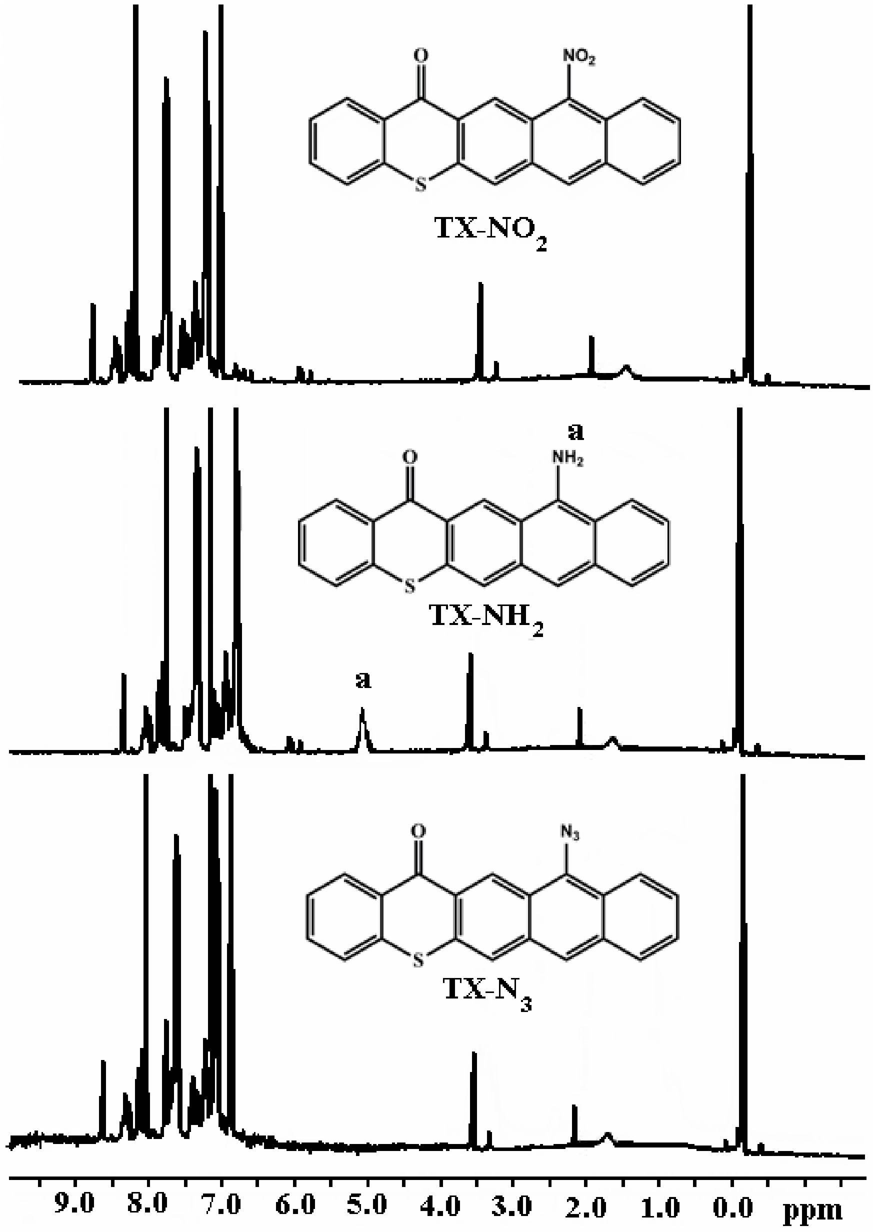


Figure 4.2 : ^{1}H NMR spectra of TX-A, TX-A-NO_2, TX-A-NH_2 and TX-A-N_3.

Additionally, FT-IR spectra of the related compounds confirm the expected structures. TX-A-NO_2 exhibits strong symmetric and asymmetric *v*N-O peaks at 1348 and 1527 cm^{-1} (Fig. 4.3). These peaks disappear completely after reduction and new broad symmetric and asymmetric *v*N–H peaks appear at 3368 cm^{-1} and 3456 cm^{-}

[1.] After the transformation of amine groups to azide groups, a strong and new vibration centered at 2104 cm^{-1} appeared in the spectrum.

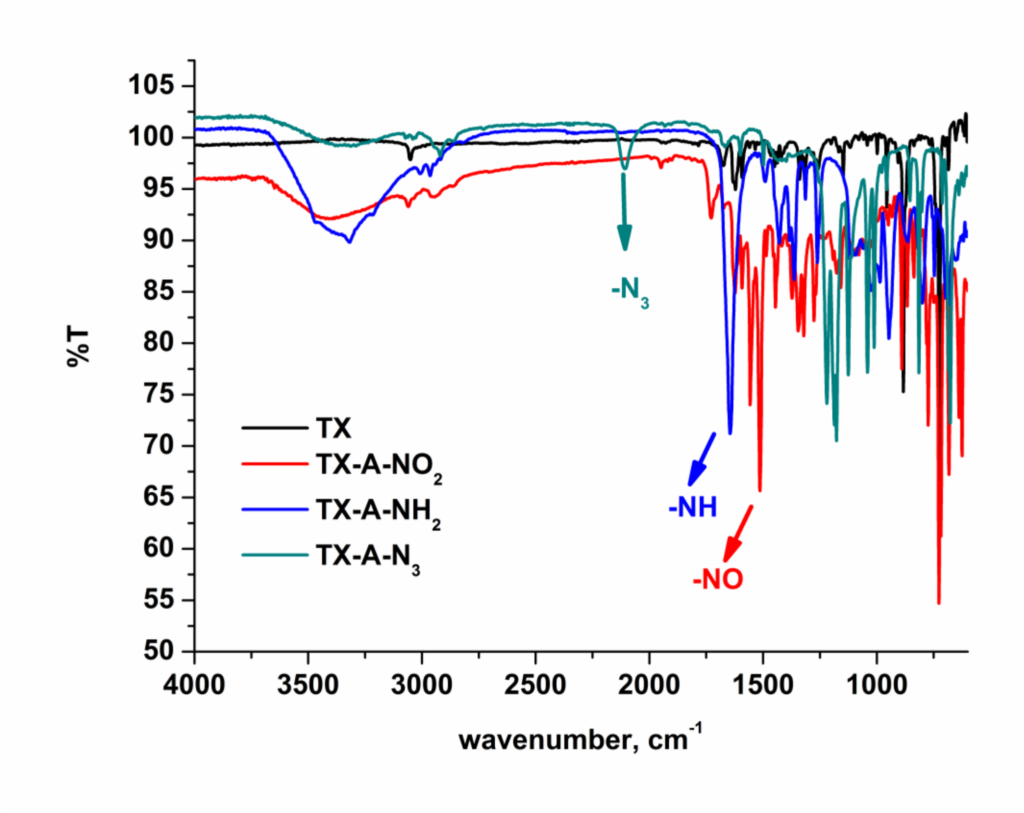


Figure 4.3 : IR spectra of TX-A, TX-A-NO_2, TX-A-NH_2 and TX-A-N_3.

As alkyne containing compounds are the other antagonist components of the click reaction we chose two different acetylene functional compounds. Thus, alkyne poly (ethyleneglycol) (Alkyne-PEG) and octyl propargyl (Oct-Pr). PEG-Pr were synthesized by a simple esterification reaction using commercially available propargyl acetic acid and poly(ethylene glycol) monomethylether. Oct-Pr was obtained by etherification process.(Figure 4.3a and 4.3b)

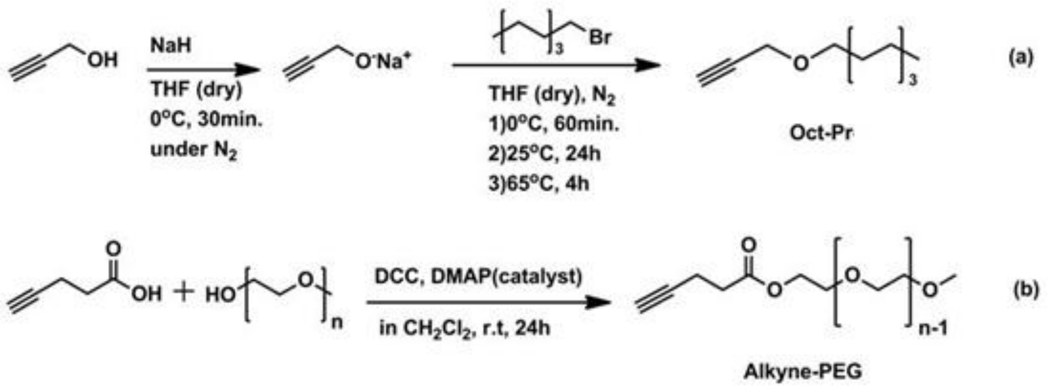


Figure 4.4 : The synthesis of (a) Oct-Pr and (b) Alkyne-PEG.

At the final step, the TX-A-N_3 was dissolved in THF and reacted with Oct-Pr and PEG-Pr in the presence of copper sulphate/sodiumascorbate in aqueous solution at room temperature. (Figure 4.5)

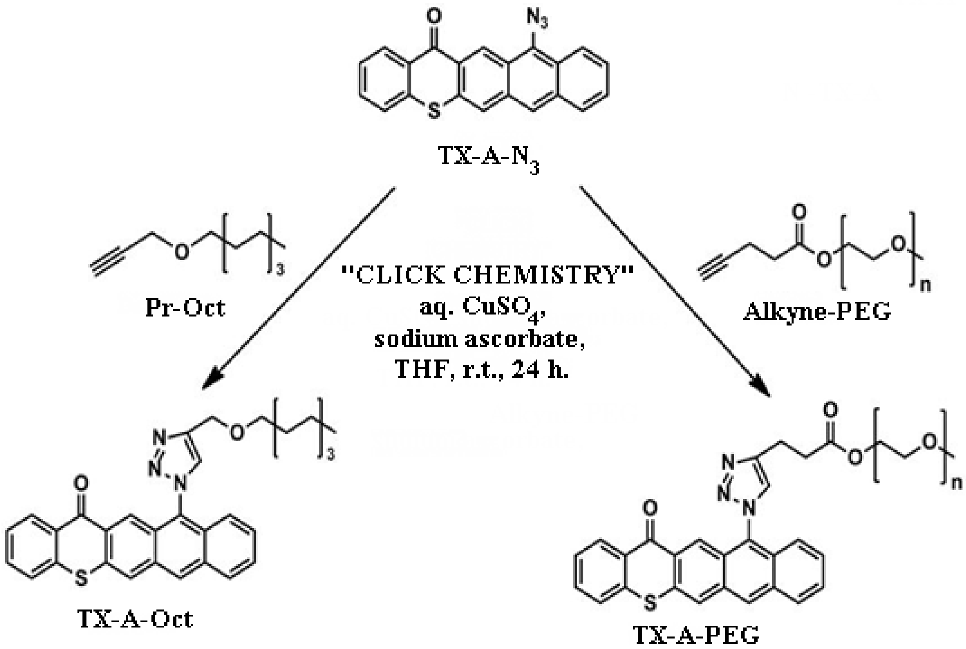


Figure 4.5 : Synthesis of photoinitiators, TX-A-PEG and TX-A-Oct.

The modification drastically changes the solubility behavior of bare TX-A. As can be seen from Table 1, TX-A-Oct and TX-A-PEG are soluble in highly polar solvents such as water and DMF as well as in the less polar solvents such as THF.

Table 4.1 : Solubility[a] of TX-A-PEG and TX-A-Oct in solvents ranked according to dielectric constants[b]

Solvent	Dielectric constant[b]	TX-A	TX-A-Oct	TX-A-PEG
Water	80	NS	S	S
DMF	38	S	S	S
CH_2Cl_2	9.1	S	S	S
THF	7.5	SS	S	S
$CHCl_3$	4.81	SS	S	S

Solubility[a] of TX-A, TX-A-Oct and TX-A-PEG in Solvents Ranked According to Dielectric Constants[b] At 25 ^oC.
S, soluble; SS, slightly soluble; NS, nonsoluble.

Evidence for occurrence of the click reactions was obtained from ^1H NMR, UV and fluorescence spectroscopy. As can be seen from Figure 4.5, where ^1H NMR spectra of TX-A-N_3, Pr-Oct and TX-A-Oct were recorded, alkyne end functionality of Pr-Oct observed at 3.4 ppm disappeared completely. Furthermore, the successful transformation of azide moieties into triazole was confirmed. Typically, in the case of TX-A-Oct, the appearance of the new methylene protons adjacent to the triazole ring at 4.3 ppm (triazole–CH_2O) and new triazole proton at 8.1 ppm and 1120cm^{-1} appear, respectively (Figure 4.6).

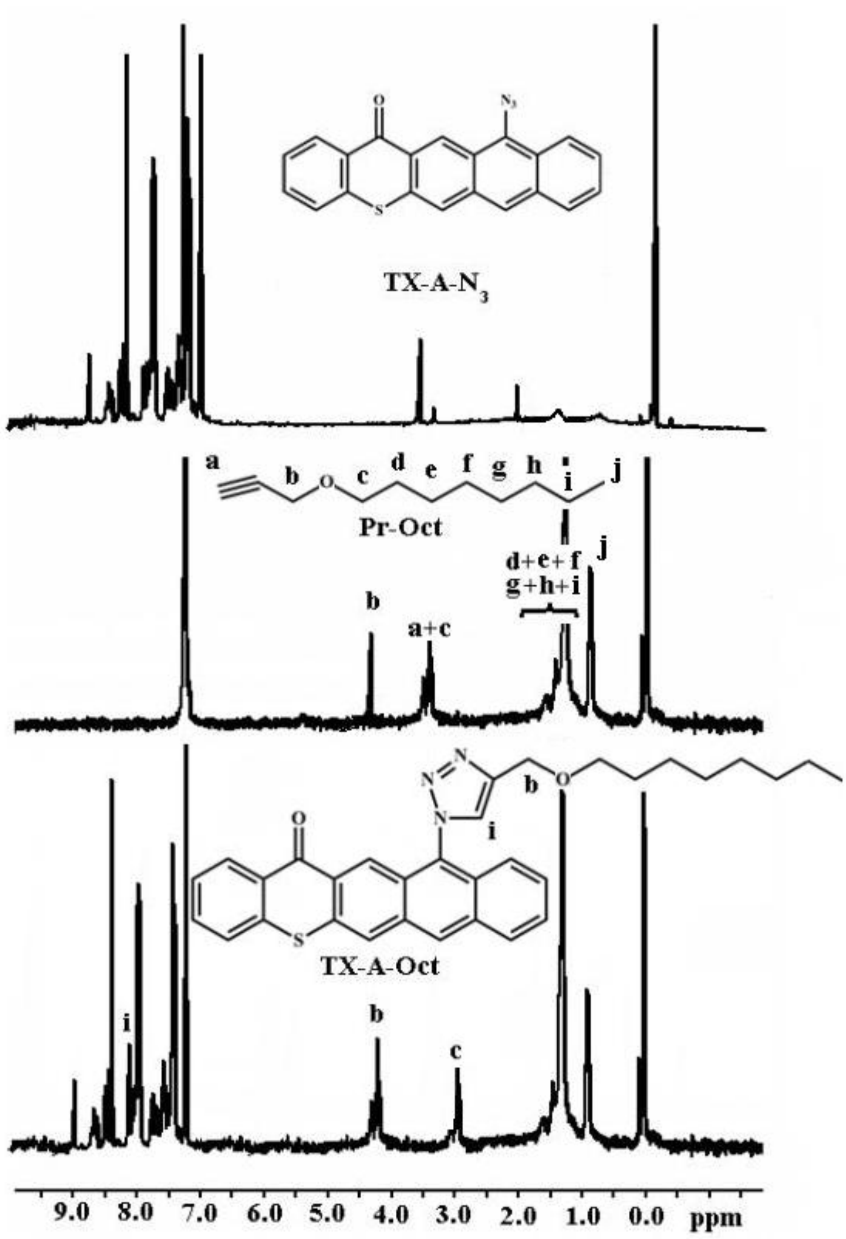


Figure 4.6 : [1]H NMR spectra of TX-A-N_3, Pr-Oct and TX-A-Oct.

The [1]H-NMR spectrum of the second photoinitiator revealed the structure of TX-A-PEG displaying characteristic peaks such as aromatic protons of TX-A between 7.4-8.5 ppm and PEG repeating unit around 3.8 ppm (-O-CH_2-). Additionally, a new triazole proton at 7.9 ppm was observed (Figure 4.8). Notably, alkyne end functionality at 1.8 ppm dissappeared completely.

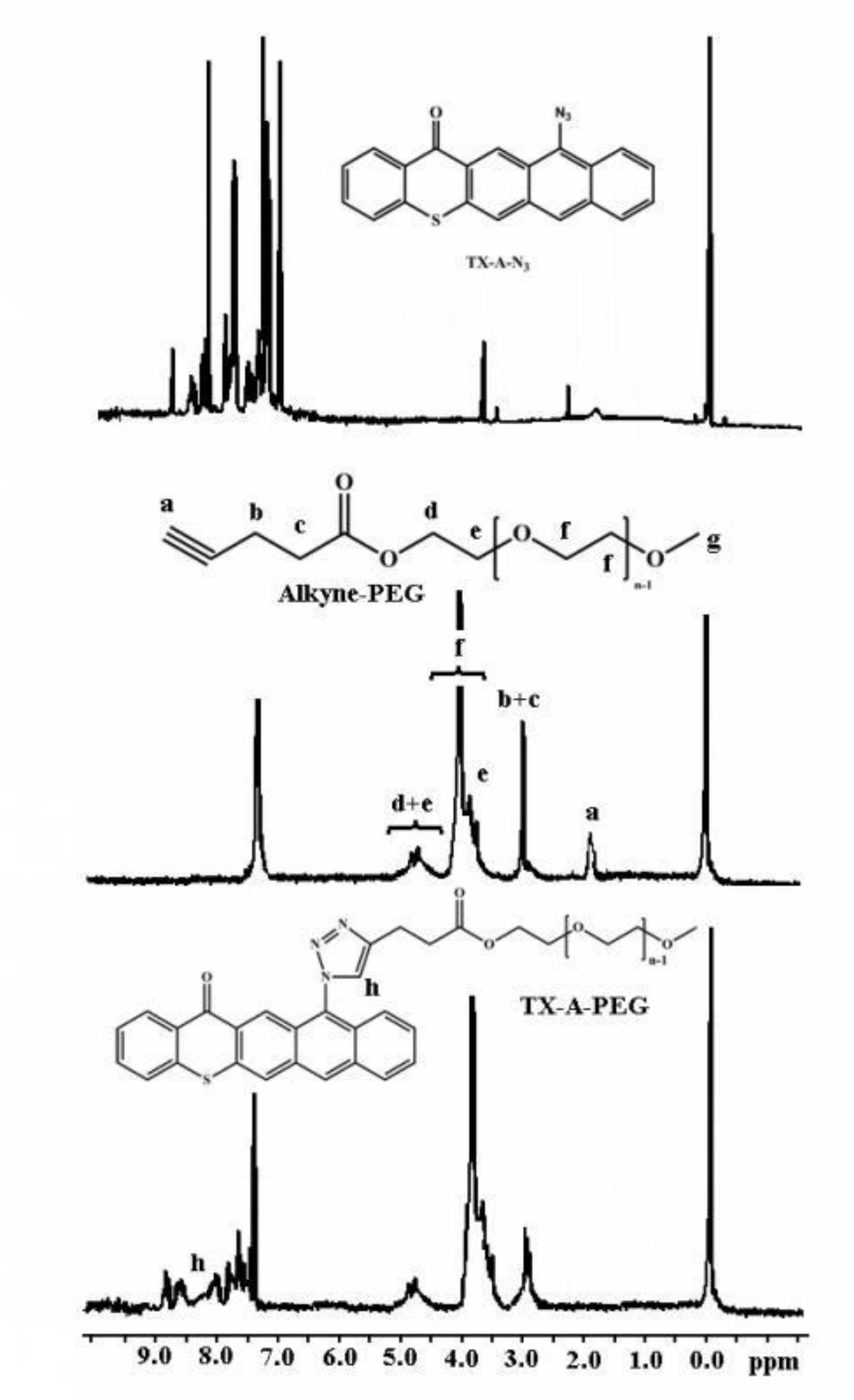


Figure 4.7 : [1]H NMR spectra of TX-A-N_3, Alkyne-PEG, TX-A-PEG in $CDCl_3$.

The FT-IR spectra also confirms quantitative reaction, as the azide stretching band at around 2104 cm^{-1} disappears completely and a new carbonyl band and an other band at 1709 cm^{-1} for both photoinitiators were noted.

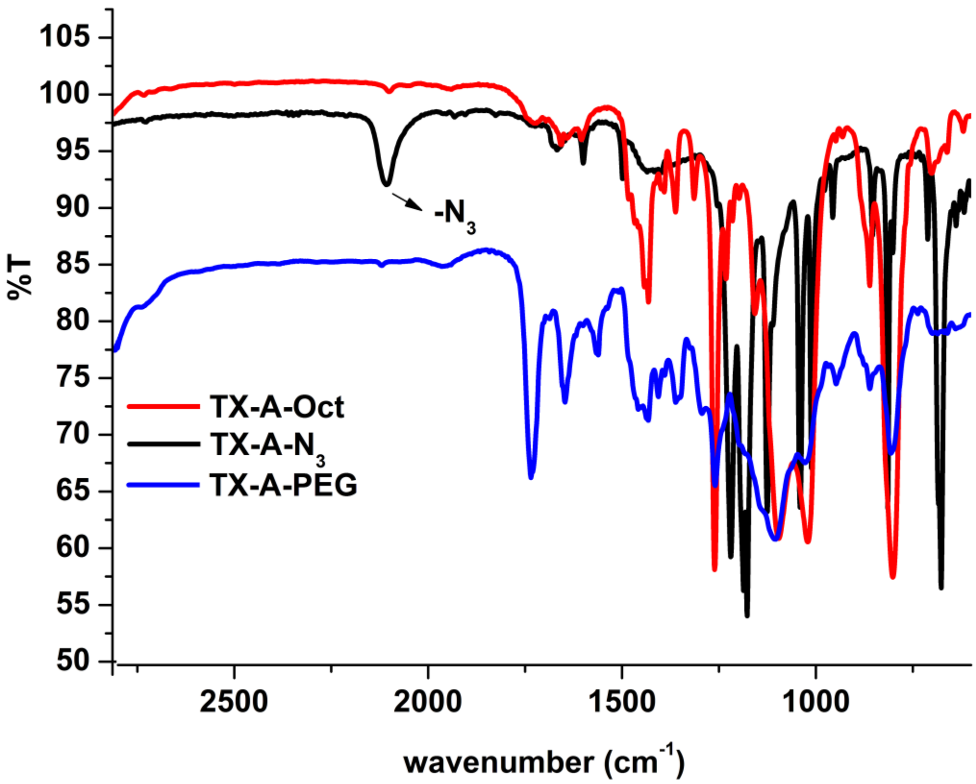


Figure 4.8 : IR spectra of TX-A-N_3, TX-A-Oct and TX-A-PEG.

Photophysical characteristics of the obtained thioxanthone compounds were investigated by UV and fluorescence spectroscopy (Figures 4.6, 4.7 and 4.8). As can be seen from Figure 4.6, TX-A displays characteristic five-finger absorbance in 300–400 nm range. Figure 4.6 demonstrates the comparison of UV spectra of TX-A-PEG and TX-A-Oct, with the parent compounds, thioxanthone (TX) and thioxanthone anthracene (TX-A). As can be seen, both new photoinitiators exhibit absorption characteristics very similar to TX-A, except a tail absorption in the visible wavelength region (λ>400 nm), where TX chromophore is transparent. Furthermore, polynuclear anthracene group has a huge effect on the absorption characteristics particularly at high wavelengths due to the extended conjugation. The substitution with longer chains may increase the contribution of the anthracene group due to the higher flexibility.

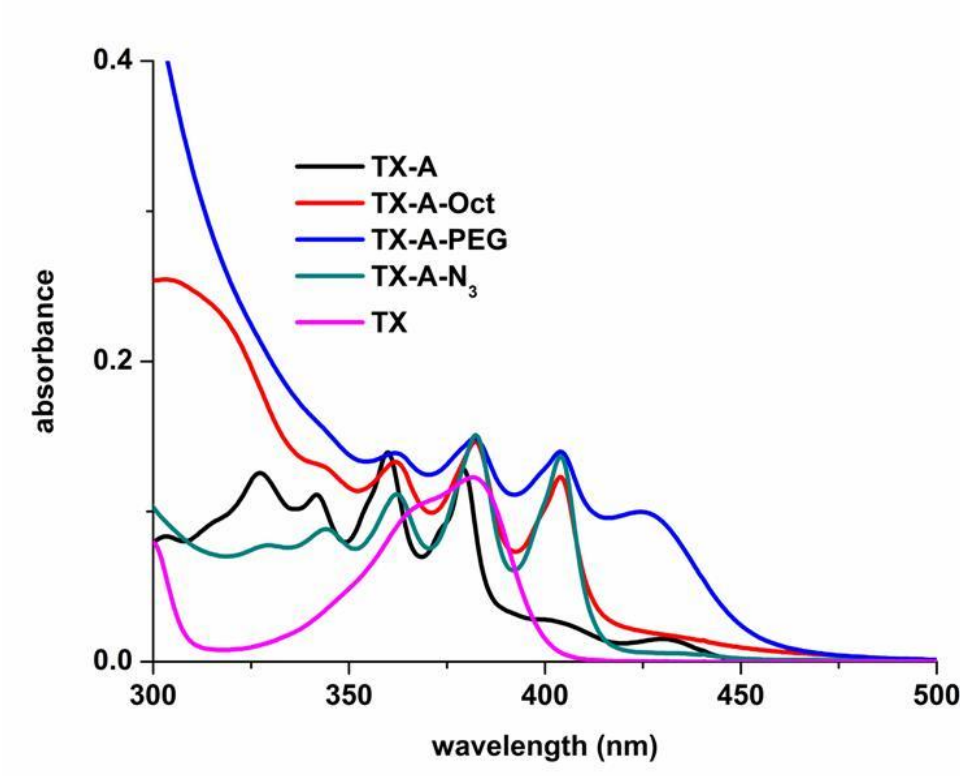


Figure 4.9 : Absorption spectra of TX, TX-A, $TX-N_3$, TX-A-Oct and TX-A-PEG in DMF. (The consentration is 1.0×10^{-5} M.)

Fluorescence spectrum of TX-A-PEG and TX-A-Oct also provides further evidence for the efficiency of the modification process and information on the nature of the excited states involved. As can be seen from Figure 4.7 and 4.8, excitation and emission fluorescence spectra in DMF of TX-A-PEG and TX-A-Oct, respectively, are almost the same. Both spectra show a nearly mirror-image-like relation between absorption and emission again similar to bare A (Anthracene), indicating its dominant photoexcited (singlet) state in the photoinitiator.

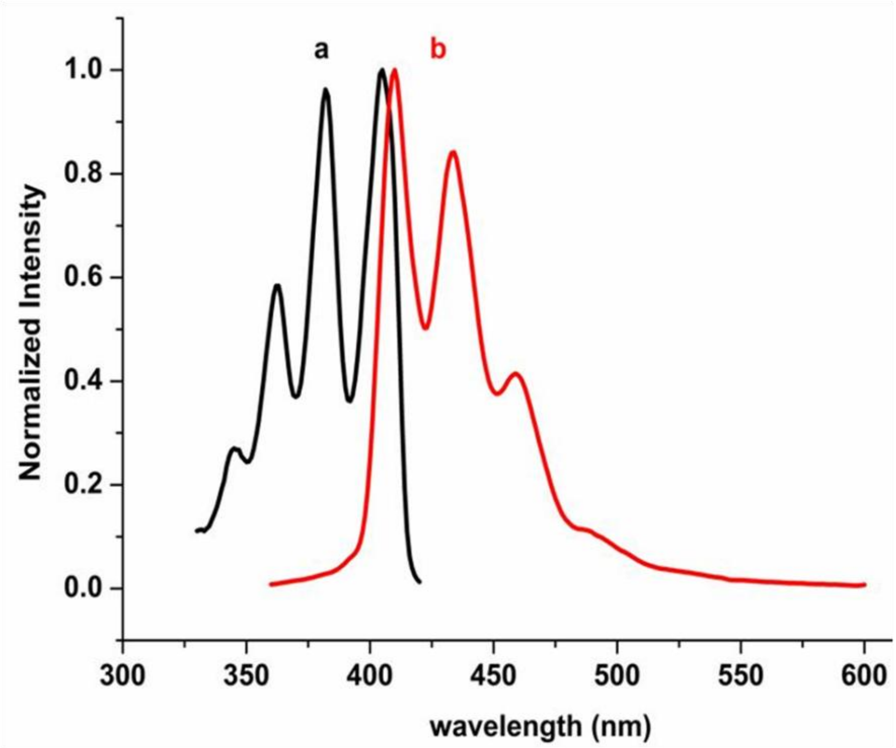


Figure 4.10 : Fluorecsence excitation (a) and emission (b) spectra of TX-A-PEG in DMF; λ_{exc} = 350nm. The consentration is 1.4×10^{-4} M.

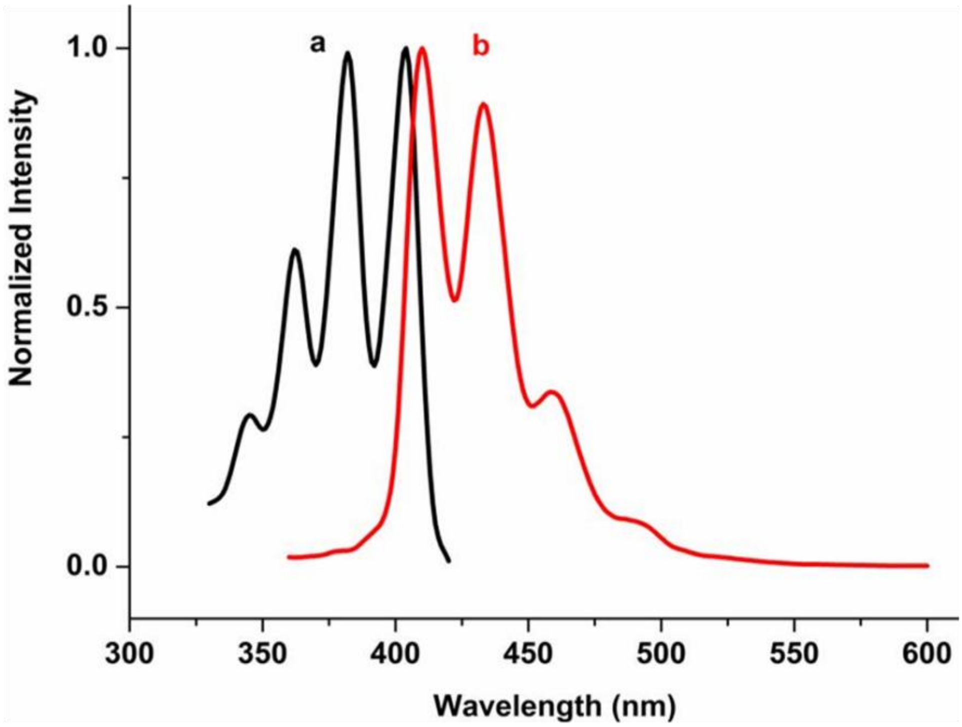


Figure 4.11 : Fluorecsence excitation (a) and emission (b) spectra of TX-A-Oct in DMF; λ_{exc} = 350nm. The consentration is 1.4×10^{-4} M.

4.2. Photopolymerization Using TX-A-Oct and TX-A-PEG

TX-A-Oct and TX-A-PEG were used photoinitiator for the polymerizations of various monomers including methylmetacrylate (MMA), acrylamide (AAM), buthylacrylate (BA), and Styrene (St) in the presence and absence of air and also hydrophilic vinyl monomers such as acrylamide (AAm). The results are compiled in Table 4.2. The overall reaction pathways are depicted in Figure 4.12 and Figure 4.13.

Table 4.2 : Photoinitiated polymerizations of MMA^a, BA^b, AAM^c and St^d in bulk.

RUN	**PI (5×10^{-3} mol L^{-1})**	**M**	**TEA (mol L^{-1})**	**N_2**	**^{f}Conv%**	**M_n^g $\times10^{-4}$**	**PDI^g**
1	TX-A-PEG	MMA^a	5×10^{-2}	+	9.5	5.7	2.0
2	TX-A-PEG	BA^b	5×10^{-2}	+	18	30.3	1.9
3	TX-A-PEG	AAM^c	5×10^{-2}	-	54	NS	-
4	TX-A-Oct	MMA^a	5×10^{-2}	+	5	10.1	2.2
5	TX-A-Oct	MMA^a	5×10^{-2}	-	7	2.4	1.7
6	TX-A-Oct	MMA^a	-	+	2.4	8.9	2.1
7	TX-A-Oct	BA^b	5×10^{-2}	+	30	18.1	3.3
8	TX-A-Oct	BA^b	5×10^{-2}	-	56	13.7	2.7
9	TX-A-Oct	BA^b	-	+	20	3.5	2.1
10	TX-A-Oct	AAM^c	5×10^{-2}	-	53.1	NS^h	-
11	TX-A-Oct	AAM^c	-	-	12.2	NS^h	-
12	TX-A-Oct	St^d	5×10^{-2}	+	1	-	-

MMA^a = 9.38 mol L^{-1}, BA^b = 7.01 mol L^{-1}, AAM ^{c}= 7.2 mol L^{-1} in water,
St^d = 8.73 mol L^{-1}
İrradiation time = 90min.
^{f,g}Determined by GPC using polystyrene standards.
^{h}NS = Nonsoluable polymer

As can be seen, TX-A-Oct is efficient photoinitiators in the presence and absence of a coinitiator such as triethyl amine (TEA). Polymerization also proceeded under nitrogen, indicating the role of oxygen. Indeed, high concentrations (5×10^{-2} molL^{-1}) of TX-A-PEG and TX-A-Oct didn't work, as we can see in Table 4.3. This behavior is due to the total complete absorption of irradiation by the photoinitiator and self-quenching of the excited photoinitiator at high concentrations [52].

Table 4.3 : Photoinitiated Polymerizations of Methyl Methacrylate (MMA)[a]

RUN	PI (5×10^{-2} mol L^{-1})	Monomer (9.38 mol L^{-1})	TEA (5×10^{-2} mol L^{-1})	N_2	Result
1	TX-A-PEG	MMA	+	+	-
2	TX-A-PEG	MMA	+	-	-
3	TX-A-PEG	MMA	-	+	-
4	TX-A-PEG	MMA	+	-	-
5	TX-A-Oct	MMA	+	+	-
6	TX-A-Oct	MMA	+	-	-
7	TX-A-Oct	MMA	-	+	-
8	TX-A-Oct	MMA	+	-	-

Irradiation time = 90min.

Obtained all datas and experiment results provided these proposed mechanisms of photoinitiators. (Figure 4.12 and 4.13)

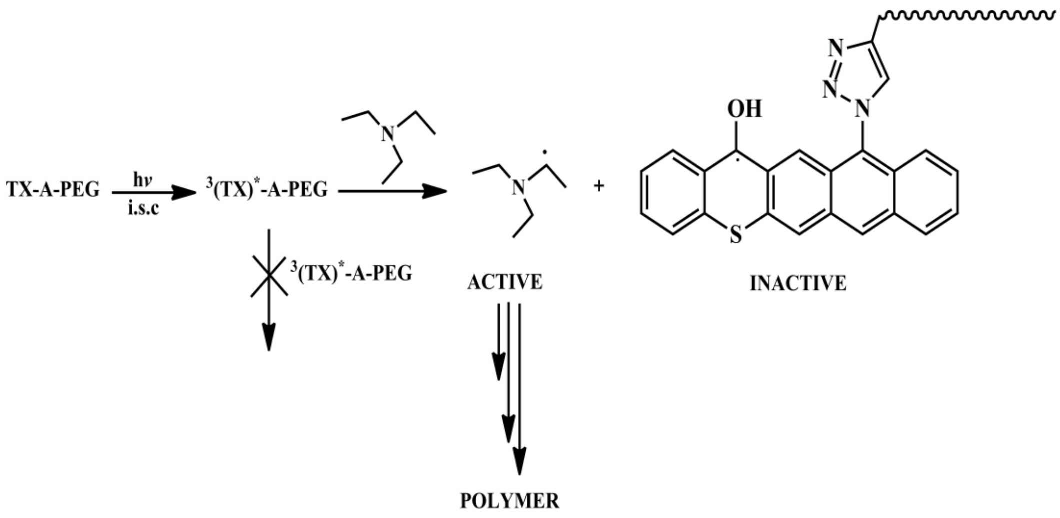


Figure 4.12 : Possible Mechanisms for photopolymerization using TX-A-PEG in the presence and absence of hydrogen donor.

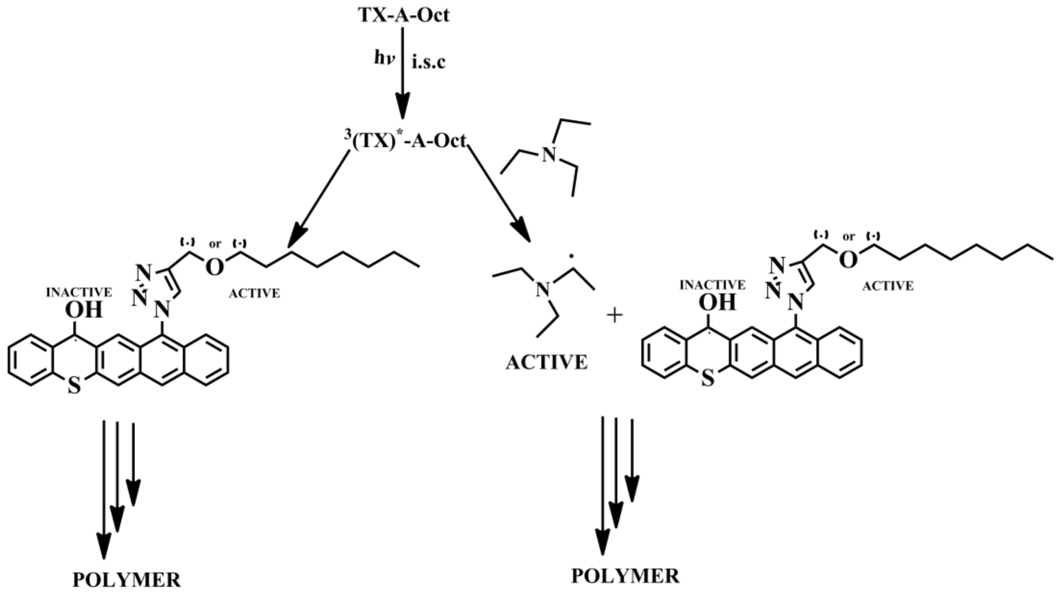


Figure 4.13 : Possible Mechanisms for photopolymerization using TX-A-Oct in the presence and absence of hydrogen donor.

Differently from mechanism of TX-A-PEG, TX-A-Oct can abstract itself hydrogen and start polymerization because of mobility of octyl- substituted group. In contrast to TX-A [15], these photoinitiators do not constitute peroxide radicals due to substituted 9- position of anthracene.

For the possibility of using the described photoinitiators in practical applications, the efficiency of TX-A-Oct and TX-A-PEG in the photocuring of formulations containing multifunctional monomers such as trimethylolpropane triacrylate (TMPTA) was also studied.

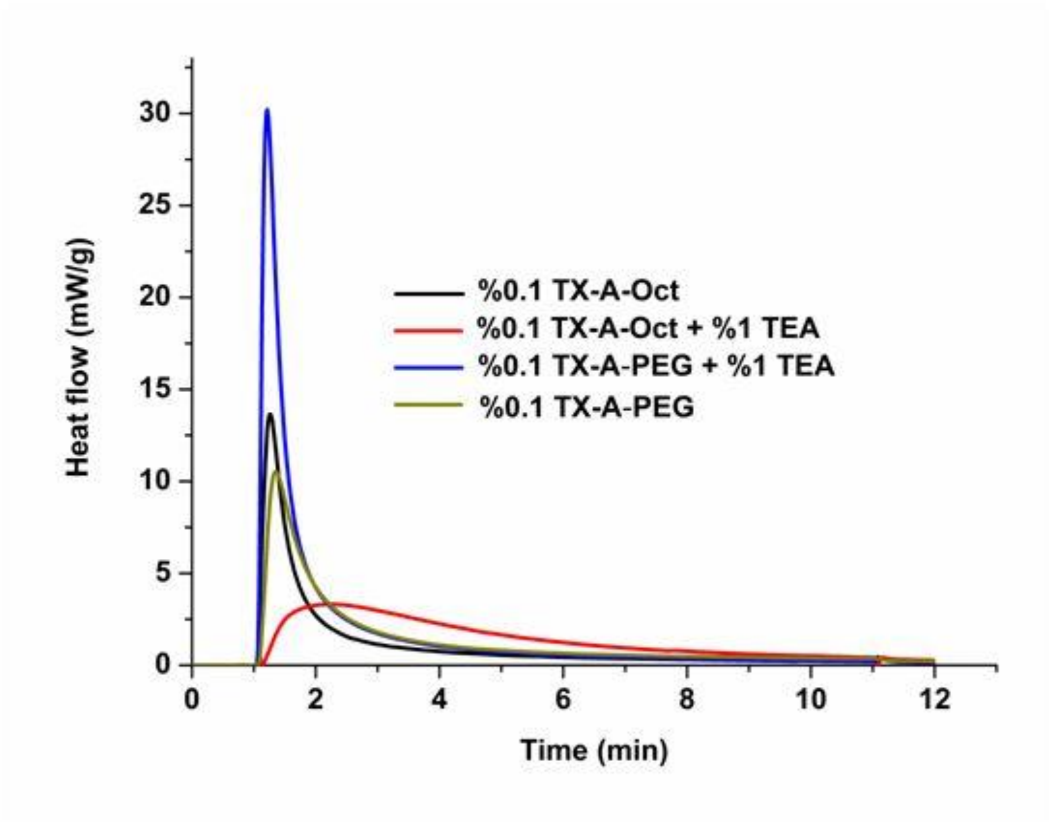


Figure 4.14 : Heat flow versus time for the polymerization of TMPTA initiated by TX-A-Oct and TX-A-PEG systems in the presence and absence of TEA cured at 30^{o}C by UV light with an intensity of 53 mW cm^{-2}. (The photoinitiator concentration is $5{\times}10^{-3}$ mol L^{-1}.)

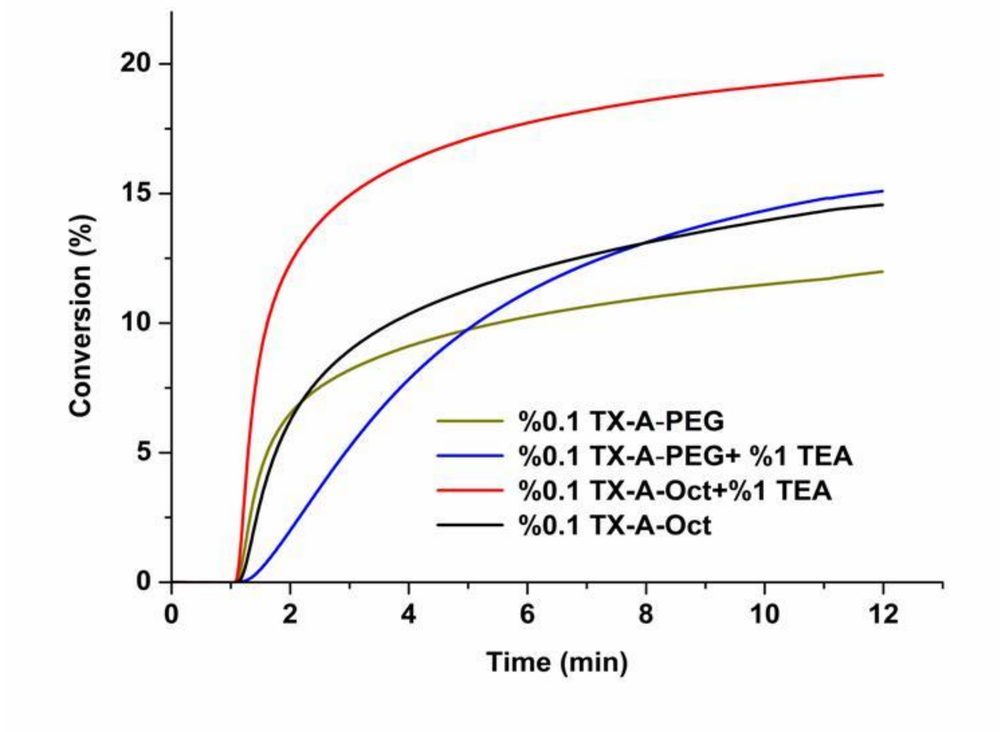


Figure 4.15 : Conversion versus time for the polymerization of TMPTA initiated by TX-A-Oct and TX-A-PEG systems in the presence and absence of TEA systems cured at 30^0C by UV light with an intensity of 53 mW cm^{-2}. (The photoinitiator concentration is 5×10^{-3} mol L^{-1}.)

Comparision of Photo-DSC plots are shown in Figure 4.14 and 4.15. Figure 4.15 displays a plot of the conversion versus irradiation time derived from Figure 4.14. The results verify that TX-A-Oct and TX-A-PEG can efficiently be used in multifunctional UV curable systems. It is evident from the Figure 14 that modified photoinitiators in the presence of additonal hydrogen donor exhibit higher rate of polymerization. Further, TX-A-Oct/TEA can initiate the photopolymerization of TMPTA more efficiently than the TX-A-PEG/TEA. This behavior may be ascribed to the limited mobility because the addition of the polymeric photoinitiator to the formulation leads to an increase in the viscosity of the formulation to a far greater extent than for its low molecular weight counter parts [53].

5. CONCLUSION

In this thesis, we have shown that TX-A based photoinitiators can readliy be modified by ’click’’ chemistry as demostrated on the example octyl and PEG substituents. The obtained photoiniators preserves the absorption characterisitcs and exhibit similar photophysical properties to the precursor TX-A photoinitiator. Moreover, such modification increases their solublity and photoinitiators are soluble in most vinyl monomers, organic solvents as well as water. It was also shown that TX-A-Oct and TX-A-PEG are efficient photoinitiators for free radical polymerization in bulk.

REFERENCES

[1] **Pappas, S. P.** *UV Curing Science and Technolgy*; Technology Marketing Corp. Norwalk, CT, 1978.

[2] **Fouassier, J. P.** *Photoinitiation, Photopolymerization and Photocuring*; Hanser Verlag: Munich, 1995.

[3] **Dietliker, K.** *Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints;* SITA Technology Ltd.: London, 1991; **Vol. III.**

[4] **Davidson, R. S.** *Exploring the Science, Technology and Applications of UV and EB Curing*; SITA Technology Ltd.: London, 1999.

[5] **Mishra, M. K.; Yagci, Y**. *Handbook of Radical Vinyl Polymerization*; Marcel Dekker: New York, 1998; Chapter 7.

[6] **Arsu, N.; Reetz, I.; Yagci, Y.; Mishra, M. K.** Chapter 8. *In Handbook of Vinyl Polymers: Radical Polymerization, Process, and Technology, 2nd ed.;* Mishra, M. K., Yagci, Y., Eds.; CRC Press: Boca Raton, FL, 2009; pp 141-204.

[7] **Davidson, R. S**. In Advances in Physical Chemistry; Bethel, D., Gold, V., Eds.; *Academic Press*: London, 1983.

[8] **Ledwith, A.; Bosley, J. A.; Purbrick, M. D. J**. Oil Colour, *Chem. Assoc.* 1978, **61,** 95–104.

[9] **Ledwith, A.; Purbrick, M. D.** *Polymer* 1973, **14,** 521–522.

[10] **Yilmaz, G, Aydogan B, Temel G, Arsu N, Moszner N, Yagci Y** 2010.Thioxanthone-Fluorenes as Visible Light Photoinitiators for Free Radical Polymerization. *Macromolecules,*: **43,** 4520-4526.

[11] **Zhao, R.; Lind, J.; Merenji, A; Eriksen, T. E.** *J Appl Chem Soc* 1984, **32,** 12010.

[12] **Ho, O.; Matsuda, M.** *J Appl Chem Soc* 1979, **101**, 5731.

[13] **Cokbaglan, L., Arsu, N., Yagci, Y., Jockusch, S. And Turro, N. J.,** 2003. 2-Mereaptothioxanthone as a Novel Photoinitiator for Free Radical Polymerization. *Macromolecules*, **36(8),** 2649-2653.

[14] **Karasu F, Arsu N, Yagci Y** 2-mercapto thioxanthone as a chain transfer agent in free-radical polymerization: A versatile route to incorporate thioxanthone moieties into polymer chain-ends.. *Journal of Applied Polymer Science,* 2007:**103(6):**3766 3770.

[15] **Balta, D. K., Arsu, N., Yagci, Y., Jockusch, S. And Turro, N. J.,** 2007. Thioxanthone-Anthracene: A New Photoinitiator for Free Radical Polymerization in the Presence of Oxygen. *Macromolecules,* **40(12),** 4138-4141.

[16] **Yilmaz G, Tuzun A, Yagci Y.** Thioxanthone–carbazole as a visible light photoinitiator for free radical polymerization. *Journal of Polymer Science Part A:Polymer Chemistry,* 2010: **48(22),** 5120-5125.

[17] **Akat H, Gacal B, Balta DK, Arsu N, Yagci Y.** Poly(ethylene glycol)-Thioxanthone Prepared by Diels–Alder Click Chemistry as One-Component Polymeric Photoinitiator for Aqueous Free-Radical Polymerization. *Journal of Polymer Science Part A: Polymer Chemistry,* 2010: **48,** 2109-2114.

[18] **Gacal B, Durmaz H, Tasdelen MA, Hizal G, Tunca U, Yagci Y, Demirel AL.** Anthracene-maleimide-based Diels-Alder "click chemistry" as a novel route to graft copolymers. *Macromolecules,* 2006:**39(16):**5330-5336.

[19] **Huisgen, R**. In 1,3-Dipolar Cycloaddition Chemistry; Padwa, A., Ed.; *Wiley*: New York, 1984; **Vol. 1**, pp 1-176.

[20] **Mishra, M. K., O.Nuyken, Kobayashi, S., Yagci, Y. and Sar, B. Schnabel, W.,** 1995. In *Macromolecular Engineering: Recent Advances,* , Eds. Plenum Press, New York.

[21] **Vazquez, B., Levenfeld, B. and Roman, J. S.,** 1998. Role of Amine Activators on the Curing Parameters, Properties and Toxicity of Acrylic Bone Cements. *Polymer International,* **46(3),** 241-250.

[22] **Catalina, F., Tercero, J. M., Peinado, C., Sastre, R., Mateo, J. L. and Allen, N. S.,** 1989. Photochemistry and Photopolymerization Study on 2-Acetoxy and Methyl-2-Acetoxy Derivatives of Thioxanthone as Photoinitiators. *Journal of Photochemistry and Photobiology a-Chemistry,* **50(2),** 249-258.

[23] **Aydin, M., Arsu, N. and Yagci, Y.,** 2003. One-Component Bimolecular Photoinitiating Systems, 2 - Thioxanthone Acetic Acid Derivatives as Photoinitiators for Free Radical Polymerization. *Macromolecular Rapid Communications,* **24(12),** 718-723.

[24] **Aydin, M., Arsu, N., Yagci, Y., Jockusch, S. And Turro, N. J.,** 2005 Mechanistic Study of Photoinitiated Free Radical Polymerizatior Using Thioxanthone Thioacetic Acid as One-Component Type II Photoinitiator. *Macromolecules,* **38(10),** 4133-4138.

[25] **Jakubiak, J., Allonas, X., Fouassier, J. P., Sionkowska, A., Andrzejewska, E., Linden, L. A. and Rabek, J. F.,** 2003. Camphorquinone-Amines Photoinitating Systems for the Initiation of Free Radical Polymerization. *Polymer,* **44(18),** 5219- 5226.

[26] **Binder, W.H. and Sachsenhofer, R.**, 2007. ‘Click’ Chemistry in Polymer and Materials Science, *Macromol. Rapid Commun*., **28**, 15-54.

[27] **Kolb, C.H.,Finn, M.G. and Sharpless, K.B.**, 2001. Click Chemistry: Diverse Chemical Function from a Few Good Reactions,*Angew. Chem. Int.,* **40**, 2004 – 2021.

[28] **Malkoch, M., Thibault, R.J., Drockenmuller, E., Messerschmidt, M., Voit, B., Russell, T.P, and Craig J. Hawker,** 2005. Orthogonal Approaches to the Simultaneous and Cascade Functionalization of Macromolecules Using Click Chemistry, *J. Am. Chem. Soc,* **127,** 14942-14949.

[29] **Kolb, H.C. and Sharpless, K.B.,** 2003. The growing impact of click chemistry on drug discovery, *Drug Discovery Today*, **8**,1128-1137.

[30] **Himo, F., Lovell, T., Hilgraf, R., Rostovtsev V., Noodleman, L., Sharpless, K.B. and Fokin, V.V**,2005. Copper(I)-Catalyzed Synthesis of Azoles. DFT Study Predicts Unprecedented Reactivity and Intermediates *J. Am. Chem. Soc.*, **127,** 210 -216.

[31] **Himo, F., Demko, Z.P., Noodleman, L. and Sharpless, K.B**,2002. Mechanisms of Tetrazole Formation by Addition of Azide to Nitriles *J. Am.Chem. Soc.*, **124**, 12210-12216.

[32] **Binder, W.H. and Kluger, C.,**, 2006. **Azide/Alkyne-“Click Reactions”: Applications in Material Science and Organic Synthesis,** *Curr.Org. Chem.*, **10**, 1791-1815.

[33] **Wang, Q., Chittaboina, S. and Barnhill, H.N**, 2005. Advances in 1,3-Dipolar Cycloaddition Reaction of Azides and Alkynes – A Prototype of “Click” Chemistry *Lett. Org., Chem.*, **2**, 293-301.

[34] **Köhn, M. And Breinbauer, R.,** 2004. **Die Staudinger-Ligation-ein Geschenk für die Chemische Biologie,** *Angew. Chem.*, **116**, 3168-3178.

[35] **Kiskan, B., Gacal, B., Tasdelen, M.A., Colak, D. And Yagci, Y.,** 2006. Design and Synthesis of Thermally Curable Polymers with Benzoxazine Fuctionalities, *Macromol. Symp.*, **245**, 27-33.

[36] **Fleischmann, S., Komber, H., Appelhans, D. and Voit, I.B**., 2007. Synhesis of Functionalized NMP Initiators for Click Chemistry: A Versatile Method for the Preparation of Functionalized Polymers and Block Copolymers, *Macromolecular Chemistry and Physics*, **208**, 1050-1060.

[37**] Huisgen, R. ,Szeimies, G., Mobius L.,** 1967. General Review,*Chem. Ber.* , **100** 2494-2501.

[38] **Lewis, W., Magallon, F.G., Fokin, V.V. and Finn, M.G,** 2004. Discovery and Characterization of Catalysts for Azide-Alkyne Cycloaddition by Fluorescence Quenching *J. Am. Chem. Soc.*, **126**, 9152- 9153.

[39] **Molteni, G., Bianchi, C.L,Marinoni, G.,Santo, N. and Ponti, A**.,2006.Cu/Cu-oxide nanoparticles as catalyst int the “click” azide-alkyne cycloaddition *New.J. Chem.,***30**, 1137.

[40] **Chan, T.R, Hilgraf, R., Sharpless, K.B. and Fokin, V.V**,2004. Polytriazoles as Copper(I)-Stabilizing Ligands in Catalysis, *Org.Lett.*, **6**, 2853-2855.

[41] **Huisgen, R**.,1989. Kinetics and reaction mechanisms: selected examples from the experience of forty years, *Pure Appl. Chem.*, **61**, 613.

[42] **Lwoski, W**., 1984. 1,3-Dipolar Cycloaddition Chemistry, *Wiley*, **Vol. I**, Chapter 5, New York

[43] **Huisgen**,**R**., 1988. Advances in Cycloaddition, Vol. I, pp. 1–31.Eds., D. P. Curran, D. Regnat, E. Peters, K. Peters, H. G. von Schnering., *JAI Press*, London.

[44] **Demko, Z. P. and Sharpless, K. B.** , 2002. A Click Chemistry Approach to Tetrazoles by Huisgen 1,3-Dipolar Cycloaddition: Synthesis of 5-Sulfonyl Tetrazoles from Azides and Sulfonyl Cyanides**,** *Angew. Chem***.** *Int. Ed***., 41,** 2110-2113.

[45] **Pachon, L.D, Maarseveen, J.H. and Rothenberg, G.,**2005**. Click Chemistry:** Copper Clusters Catalyse the Cycloaddition of Azides with Terminal Alkynes *Adv.Synth. Catal.,* **347**, 811

[46] **Lutz, J.F,** 2007. 1, 3-Dipolar Cycloadditions of Azides and Alkynes: A Universal Ligation Tool in Polymer and Materials Science, *Angew. Chem. Int.*., **46**, 1018 – 1025.

[47] **Schnabel, W, Levchik, G.F, Wilkie, C.A, Jiang, D.D. and Levchik, S.V.,**. 1999. Thermal degradation of polystyrene, poly (1, 4-butadiene) and copolymers of styrene and 1,4-butadiene irradiated under air or argon with ^{60}Co-γ-rays, *Polym Degrad Stab,* **63**, 365-375.

[48] **Decker, C., Nguyen, T. and Viet T**., 1999. Photocrosslinking of functionalized rubbers, 8. The thiol-polybutadiene system**,** *Macromol. Chem. Phys*., **200**, 1965–1974.

[49] **Jiang, D.D., Levchik, GF, Levchik, S.V and Wilkie, C.A.,** 1999**.** Cross-linking of polystyrene by Friedel–Crafts chemistry to improve thermal stability, *Polym Degrad Stab*. , **65**, 387-395.

[50] **Durmaz YY, Sangermano M, Yagci Y.** 20**10.** Surface Modification of UV-Cured Epoxy Resins by Click Chemistry. Journal of Polymer Science Part A: *Polymer Chemistry*,: **48**, 2862-2868

[51] **Andrzejewska, E.; Andrzejewski, M.** *J. Polym. Sci.*, Part A: Polym. Chem. 1998, **36**, 665–673.

[52] **Pappas, S. P.** *J. Radiat. Curing* 1987, **14**, 6-12. Resultta

[53] **Davidson, R. S.** *J. Photochem. Photobiol.*, A 1993, **69**, 263–275..

CURRICULUM VITAE

Candidate's full name : Deniz TUNC

Place and date of birth : Istanbul, 17.04.1988

Universities and Colleges attended :

2009-2010 Master of Science (Chemistry), Istanbul Technical Univesity, Istanbul, Turkey

2005-2009 Chemistry, Trakya University, Edirne, Turkey

2002-2005 Kocasinan High School, Istanbul, Turkey